

S/079/61/031/003/003/013  
B118/B207

## AUTHORS:

Shmonina, V. P., Temnikova, G. P., and Sokol'skiy, D. V.

## TITLE:

Catalytic reduction of aromatic nitro compounds. X. Effect of phenol hydroxyl upon the reduction kinetics of the nitro group in nitrobenzene derivatives

## PERIODICAL:

Zhurnal obshchey khimii, v. 31, no. 3, 1961, 743-749

TEXT: The present paper describes the effect exerted by the presence and position of phenol hydroxyl upon the reduction kinetics of the nitro group in isomeric nitrophenols in the presence of a nickel or platinum catalyst, i. e., in neutral or alkaline-aqueous alcoholic media. The phenol hydroxyl and ONa groups that were introduced into the nitro-compound molecule reduce its adsorption on both catalysts more intensively in ortho-position than in para-position where the reduction is greater than in meta-position. When the reaction is carried out on the skeleton nickel catalyst in an alkaline medium, the ONa group in the molecule of the nitro compound accelerates the reduction. Thus, the compounds studied may, with respect to the increase of reaction rate, be classified as follows: nitrobenzene, m-nitrophenolate, ✓

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✓

Catalytic reduction ...

p-nitrophenolate, o-nitrophenolate. On the platinum catalyst, however, the ONa group retards the reduction of the nitro compound, and the order of compounds is inverse with respect to the increase of reaction rate. In a neutral medium, the bond between hydrogen and platinum is less stable so that the position of phenol hydroxyl in the molecule exerts no essential influence upon the reaction rate. There are 6 figures, 4 tables, and 8 Soviet-bloc references.

ASSOCIATION: Kazakhskiy gosudarstvennyy universitet (Kazakh State University)

SUBMITTED: January 28, 1960

Card 2/2

TEMNIKOVA, L.F.

Pa

15-

Absorption of phosphoric acid by the solonetzic soils (saline soils). L. F. Temnikova. Uchenye Zapiski Naukovedcheskogo Instituta po Chernozemstvu i Solonetzam. Vyp. V. G. Chernozemstvo, Stolbtsy. Vsesoyuznyi Nauk.-Tekhn. Institut po Chernozemstvu i Solonetzam. 1940, No. 1. Ch. 1. Salonetzic soils absorb P<sub>2</sub>O<sub>5</sub> to a smaller degree than do other soils. The P<sub>2</sub>O<sub>5</sub> horizon of the solonetzic soils does not differ greatly from the A horizon in its ability to bind P<sub>2</sub>O<sub>5</sub>, in spite of the large content of sesquioxides (FeO<sub>3</sub>). In this it differs from the red soils and from latrites. This is explained by the amphotropic behavior of FeO<sub>3</sub> under the influence of the pH of the medium. Humus cannot bind P<sub>2</sub>O<sub>5</sub> in large amounts. Normal amounts of P fertilizers have a large effect on the solonetzic soils. The mixing of A and P<sub>2</sub>O<sub>5</sub> horizons has very little effect on the absorption of P<sub>2</sub>O<sub>5</sub>. Seven references. W. R. Thom

SHKILEV, V. V.; TEPNIKOVA, L. Y.

Case of importation of black rats into the city of Ussuriysk.  
Izv. Irk.gos.nauch.-issel.protivochum.inst. 19:98-100 '58.  
(MIRA 13:7)  
(Ussuriysk--Rats)

COUNTRY : USSR  
CATEGORY : Cultivated Plants. Cereals. X

ABS. JOUR. : RZhBiol., No. 1958, No. 10464.

AUTHOR : Temnikova, N.  
INST. : Academy of Sciences, Latvian SSR  
TITLE : Experiments in Growing Corn in Latvia under the Meteorological Conditions of 1955.

ORTG. PUB. : Latv. PSR zinatnu Akad. vestis, Izv. AN Latv. SSR, No. 2. 57-62

ABSTRACT : The simplest method for the evaluation of adequate moisture supply is Selyaninov's "hydrothermal coefficient" (HTC). In regard to HTC, Latvian Republic has to be assigned to the zone of excessive precipitation. Experiments in growing corn were conducted at 13 points in the Republic. The milky stage of maturity came on 12 plots in the second and third 10-day period of September. For Osetinskaya variety, the weight of the green roughage varied from 377 to 1104 centners/ha. The relation of the

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COUNTRY :	M
CATEGORY :	
ABS. JOUR. :	RZhBiol., No. 23, 1958, No. 104644
AUTHOR :	
INST. :	
TITLE :	
ORIG. PUB. :	
ABSTRACT :	height of corn to the value of HTC was determined. This makes it possible to evaluate objectively one or another experimental point in regard to corn growing, and to evaluate the feasibility of the profitability of corn production for green roughage in the individual rayons of Latvian SSR with the first approximation of climatic forecast. --O. V. Yakushkina
Card: 2/2	

PHASE I BOOK EXPLOITATION SOV/4761

Kozyreva-Aleksandrova, L.S., and N.I. Temnikova

Radioaktivnyy izotop yoda J<sup>131</sup> (Radioactive Isotope of Iodine J<sup>131</sup>)  
Moscow, Atomizdat, 1960. 21 p. 15,000 copies printed.

Ed.: G.M. Pchelintseva; Tech. Ed.: N.A. Vlasova.

PURPOSE: This booklet is intended for scientific personnel working with radioactive isotopes, particularly for those interested in methods of extracting J<sup>131</sup>.

COVERAGE: The authors note the increasingly wider application of radioisotopes in science and industry, and review the theory of radioisotopes as developed in this century. The following are discussed briefly: chemical methods of extracting J<sup>131</sup>, the extracting of J<sup>131</sup> with the carrier from irradiated tellurium, methods of extracting carrier-free J<sup>131</sup>, the extraction of J<sup>131</sup> from neutron-irradiated tellurium, the applications of radioactive J<sup>131</sup>, and safety

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Radioactive Isotope of Iodine  $I^{131}$

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engineering and technique in working with the radioactive iodine. No personalities are mentioned. There are 15 references, all Soviet.

TABLE OF CONTENTS: None given

AVAILABLE: Library of Congress (QD466.5I1K8)

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JA/wrc/gmp  
3-29-61

TEMNIKOVA, N.S.

O. Gee

Meteorological Abst.  
Vol. 4 No. 3  
March 1953  
Part 2  
Bibliography on  
Frost and Frost  
Forecasting

4C-217 ✓ 551.524.17(374)  
Temnikova, Natalia S. Tipizatsiya zamorozkov Evropeiskoi territorii Soinza, ikh dlitel'nost' i  
povtorizemost'. [Classification of frosts in European U.S.S.R., their duration and frequency.]  
*Meteorologiya i Gidrologiya*, 4(6):26-44, June 1938. 13 figs., 25 nota. DLC - On the basis of observa-  
tions during 1891-1915, the author analyzes the conditions under which spring and autumn frosts  
form and establishes seven types of frost situations. The advection of cold air or polar air  
masses causes frosts. Their duration also depends on synoptic processes. Numerous charts illus-  
trate synoptic situations, duration, frequency and distribution (seasonal and geographic) of frost.  
Subject Heading: 1. Frost distribution 2. Frost duration 3. Frost frequencies 4. Long period  
records 5. Synoptic conditions for frost 6. European U.S.S.R. -

TEMNIKOVA, H.S., kandidat geograficheskikh nauk

A rare instance of surface inversion. Metero. i gidrol. no.2:  
28-30 F '53. (MIRA 8:9)

1. Rostovskoye UGMS  
(Atmospheric temperature)

TEMNIKOVA, N.S.

FEDOROV, Ye.Ye., professor; PREDTECHENSKIY, P.P.; BUCHINSKIY, I.Ye.; SEYANINOV, G.T., professor; BOSHNO, L.V.; ALISOV, B.P.; BIRYUKOV, N.N.; GAL'TSOV, A.P.; GRIGOR'IEV, A.A., akademik; EYGENSON, M.S., professor; MURETOV, N.S.; KHROMOV, S.P.; BOGDANOV, P.N.; LEBEDEV, A.N.; SOKOLOV, V.N.; YANISHEVSKIY, Yu.D.; SAMOYLENKO, V.S.; USMANOV, R.F.; CHUBUKOV, L.A.; TROTSENKO, S.Ya.; VANGENGESYM, G.Ya.; SOKOLOV, I.F.; STYRO, B.I.; TEMNIKOVA, N.S.; ISAYEV, E.A.; DMITRIYEV, A.A.; MALYUGIN, Ye.A.; LIEDEMAA, Ye.K.; SAPOZHNIKOVA, S.A.; RAKIPOVA, L.R.; POKROVSKAYA, T.V.; BAGDASARYAN, A.B.; ORLOVA, V.V.; RUVINSKAYA, Ye.S., professor; MILEVSKIY, V.Yu.; SHCHERBAKOVA, Ye.Ya.; BOCHKOV, A.P.; ANAPOL'SKAYA, L.Ye.; DUNAYEVA, A.V.; UTESHEV, A.S.; HUDENEVA, A.V.; RUDENKO, A.I.; ZOLOTAREV, M.A.; NERSESYAN, A.G.; MIKHAYLOV, A.N.; GAVRILOV, V.A.; TSOMAYA, T.I.; DEVYATKOVA, A.M.; ZAVARINA, M.V.; SHMETER, S.M.; BUDYKO, M.I., professor.

Discussion of the report (in the form of debates) [of the current state climatological research and methods of developing it]. Inform. (MIRA 8:3) sbor.GUGMS no.3/4:26-154 '54.

1. Chlen-korrespondent Akademii nauk SSSR (for Fedorov). 2. Glavnaya geofizicheskaya observatoriya im. A.I. Voeykova (for Predtechenskiy, Lebedev, Yanishevskiy, Isayev, Rakipova, Pokrovskaya, Orlova, Rubinshteyn, Budyko, Shcherbakova, Anapol'skaya, Dunayeva, Rudneva, Gavrilov, Zavarina). 3. Ukrainskiy nauchno-issledovatel'skiy gidrometeorologicheskiy institut (for Buchinskiy).

(Continued on next card)

FEDOROV, Ye.Ye., professor; PREDTECHENSKIY, P.P., and others.

Discussion of the report (in the form of diskette) [of the current state climatological research and methods of developing it]. Inform. sbor. GUGMS no.3/4:26-154 '54. (Card 2) (MIRA 8:3)

4. Vsesoyuznyy institut rastenievodstva (for Selyaninov, Rudenko).
5. Bioklimaticeskaya stantsiya Kislovodsk (for Boshno). 6. Morskij gosudarstvennyy universitet im. M.V.Lomonosova (for Alisov).
7. Ministerstvo putej soobshcheniya SSSR (for Biryukov). 8. Institut geografii Akademii nauk SSSR (for Gal'tsov, Grigor'yev). 9. Geofizicheskaya komissiya Vsesoyuznogo geograficheskogo obshchestva (for Tygenson). 10. Ministerstvo elektrostantsiy i elektropromyshlennosti SSSR (for Muretov). 11. Leningradskiy gosudarstvennyy universitet im. A.A.Zhdanova (for Khromov). 12. TSentral'nyy nauchno-issledovatel'skiy gidrometeorologicheskiy arkhiv (for Sokolov, Zolotarev). 13. Gosudarstvennyy okeanograficheskiy institut (for Samoylenko). 14. TSentral'nyy institut prognozov (for Umanov, Sapozhnikova). 15. Institut geografii Akademii nauk SSSR i TSentral'nyy institut kurortologii (for Chubukov). 16. Nauchno-issledovatel'skiy institut imeni Sechenova, Yalta (for Trotsenko). 17. Arktycheskiy nauchno-issledovatel'skiy institut (for Vangengsym).

(Continued on next card)

FEDOROV, Ye.Ye., professor; PREDTECHENSKIY, P.P., and others.

Discussion of the report (in the form of debates) [of the current state of climatological research and methods of developing it].  
Inform.sbor. GUGMS no.3/4:26-154 '54. (Card 3) (MLRA 8:3)

18. Dal'nevostochnyy nauchno-issledovatel'skiy gidrometeorologicheskiy institut (for Sokolov). 19. Institut geologii i geografii Akademii nauk Litovskoy SSR (for Styro). 20. Rostovskoe upravlenie gidrometstuzhby (for Temnikova). 21. Morskoy gidrofizicheskiy Institut Akademii nauk SSSR (for Dmitriyev). 22. Vsesoyuznyy institut rasteniyevedstva (for Malyugin). 23. Akademiya nauk Estonskoy SSR (for Liedemaa). 24. Akademiya nauk Armyanskoy SSR (for Bagdasaryan). 25. Leningradskiy gidrometeorologicheskiy institut (for Milevskiy).

(Continued on next card)

FEDOROV, Ye.Ye., professor; PREDTECHENSKIY, P.P., and others.

Discussion of the report (in the form of debates) [of the current state  
climatological research and methods of developing it]. Infcrm.sbor.  
GUGMS no.3/4:26-154 '54. (Card 4) (MIRA 8:3)

26. Gosudarstvennyy gidrologicheskiy institut (for Bochkov). 27. Ka-  
zakhskiy nauchno-issledovatel'skiy gidrometeorologicheskiy institut  
(for Uteshev). 28. Upravlenie gidrometsluzhby Armyanskoy SSR (for Ner-  
sesyan). 29. Leningradskoye upravleniye gidrometsluzhby (for Mikhaylov,  
Devyatkova). 30. Tbilisskiy gosudarstvennyy universitet (for Tsomaya).  
31. TSentral'naya aerologicheskaya observatoriya (for Shmeter).  
(Climatology)

TEMNIKOVA, N.S.

AID P - 1433

Subject : USSR/Meteorology and Hydrology

Card 1/1 Pub. 71-a - 7/23

Author : Temnikova, N. S., Kandidat of Geogr. Sciences

Title : Dust storms in the Stalinograd district

Periodical : Met. i gidro., 1, 31-32, Ja - F 1955

Abstract : Statistical data are given of dust storms with a wind velocity of 12-15m/sec. from an analysis of observations taken from 1936 to 1950. Measures of protection are suggested and a table given of these storms by months observed at 7 stations for 1948 and 1949. One Russian reference

Institution: Main Administration of the Hydrometeorological Service  
at the Council of Ministers of the USSR

Submitted : No date

TEMNIKOVA, N. S.

AID P - 3182

Subject : USSR/Meteorology

Card 1/1 Pub. 71-a - 9/23

Author : Temnikova, N. S.

Title : Early frost on ploughed land and meadows

Periodical : Met. i. gidsr., 5, 38-40, 8/0 1955

Abstract : The possibility of forecasting early and late frost following 10 year observations made in Latvia is discussed. The freezing of corn at temperatures of -2°C is reported. Diagrams show the difference in temperatures of air, ploughed earth and soil covered with grass. Four diagrams.

Institution : None

Submitted : No date

14-57-6-12148

Translation from: Referativnyy zhurnal, Geografiya, 1957, Nr 6,  
p 67 (USSR)

AUTHOR: Temnikova, N. S.

TITLE: Frost Danger in Various Forms of Hilly Regions  
(Morozoopasnost' razlichnykh form kholmistogo  
rel'yefa)

PERIODICAL: Izv. AN LatvSSR, 1956, Nr 9, pp 75-83

ABSTRACT: A microclimatic survey was carried out simultaneously at 13 points in the northeastern part of the Vidzem-skaya vozvyshennost' (upland) from May 6 to June 11, 1954, during the period of the spring frosts. Results of the observations have shown that average minimum temperature (at an 0.5 m level) was 2° or 3° higher on the hill summits than in the adjacent valleys. These values were smaller on slopes than on hilltops, being only from 0.2° to 0.4°, and reached 1° only on

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14-57-6-12148

Frost Danger in Various Forms (Cont.)

the steepest slopes. The greatest difference between minimum temperatures in the valleys and on the summits, reaching 4° or 5° and even 6°, was observed during the periods of cold advection; during warm advection these differences decreased sharply. The extent of differences between these values depends also on the clouds and on the wind velocity, but steepness of a slope and its exposure have no effect on it. Regardless of the weather, the average minimum temperatures are lowest in the valleys and highest on the summits. Thermal relations over the slopes, valleys, and summits are substantially different during the periods of hot and cold advection. Regardless of whether the weather is clear, overcast or windy, the temperature differences are considerably smaller during the periods of warm advection than during the periods of cold advection.

I. D.

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TENNIKOVA, M.S.

Meteorological conditions during the solar eclipse of June 30, 1954,  
in Latvian S.S.R. Biul.VAGO no.20:12-18 '57. (ELRA 10:8)

1. Rizhskaya geofizicheskaya observatoriya.  
(Latvia--Meteorology--Observations)  
(Eclipses, Solar--1954)

SOV/50-59-5-11/22

3(7)  
AUTHOR: Temnikova, N. S.  
TITLE: Methods of Studying the Microclimate (O metodakh izucheniya mikroklimata)  
PERIODICAL: Meteorologiya i hidrologiya, 1959, Nr 5, pp 45 - 48 (USSR)  
ABSTRACT: The agroclimatic handbooks, the program of which contains a section on the microclimate, need microclimatic corrections. Up to now, the principal method of obtaining these mean microclimatic corrections has been the method of the analysis of so-called background (fonovyy) charts. This method has, however, some relevant shortcomings. It is shown here that reliable microclimatic corrections for the different meteorological elements can only be obtained at present by means of microclimatic special surveys in the different regions of the USSR. The experience of the Rizhskaya hidrometeorologicheskaya observatoriya (Riga Hydrometeorological Observatory) of the UGMS Latv. SSR (Hydrometeorological Service Administration of the Latvian SSR) shows that such surveys can be organized very easily with the forces of the hydrometeorological stations working at present. In fall 1957, the UGMS of the Estonian, Lithuanian and Latvian SSR began to carry out a

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Methods of Studying the Microclimate

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number of such surveys in the Baltics. First of all, the influence of the different forms of hill country on the climate is to be clarified. The execution of these surveys is described here in short. In the descriptions of the MCP (microclimatic points), the character of the vegetation and soil, the moisture content of the surface of the soil, the steepness and illumination of the slope, the relative superelevation above the bottom of the valley, and possibly the profile of the slope, should be indicated. The observations must be made in fall, from September 20 until the time when the mean diurnal air temperature continuously exceeds 5°, and in spring, from April 16 to June 15. According to the program described here, the regions of the Vidzem and Kurzem Elevations were investigated microclimatically in fall 1957 and in the warm period of 1958. To check the data obtained, analogous surveys were carried out by the method given here at the hydro-meteorological station of Saldus on the Kurzem Elevation. These data were evaluated by L. M. Fonina. The results were in full conformity with those obtained before. This fact shows that there are certain rules in the distribution of microclimatic corrections for the same relief forms in the same region. The microclimatic investigations of the moisture content of the soil are theoretic-

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cally very interesting and very important to practice. In this connection, it would be convenient to complete the survey program of 1958 by measurements of the soil moisture content in the upper horizon and in the arable horizon. There are 7 Soviet references.

Card 3/3

TEMNIKOVA, Natal'ya Sergeyevna; DROZDOV, O.A., prof., red.; USHAKOVA,  
T.V., red.; SERGEEV, A.N., tekhn.red.

[Climate of the Northern Caucasus and adjacent steppes] Klimat  
Severnogo Kavkaza i prilezhashchikh stepей. Pod red. O.A.Drozdov  
va. Leningrad, Gidrometeor.izd-vo, 1959. 367 p. (MIRA 13:2)  
(Caucasus, Northern--Climate)

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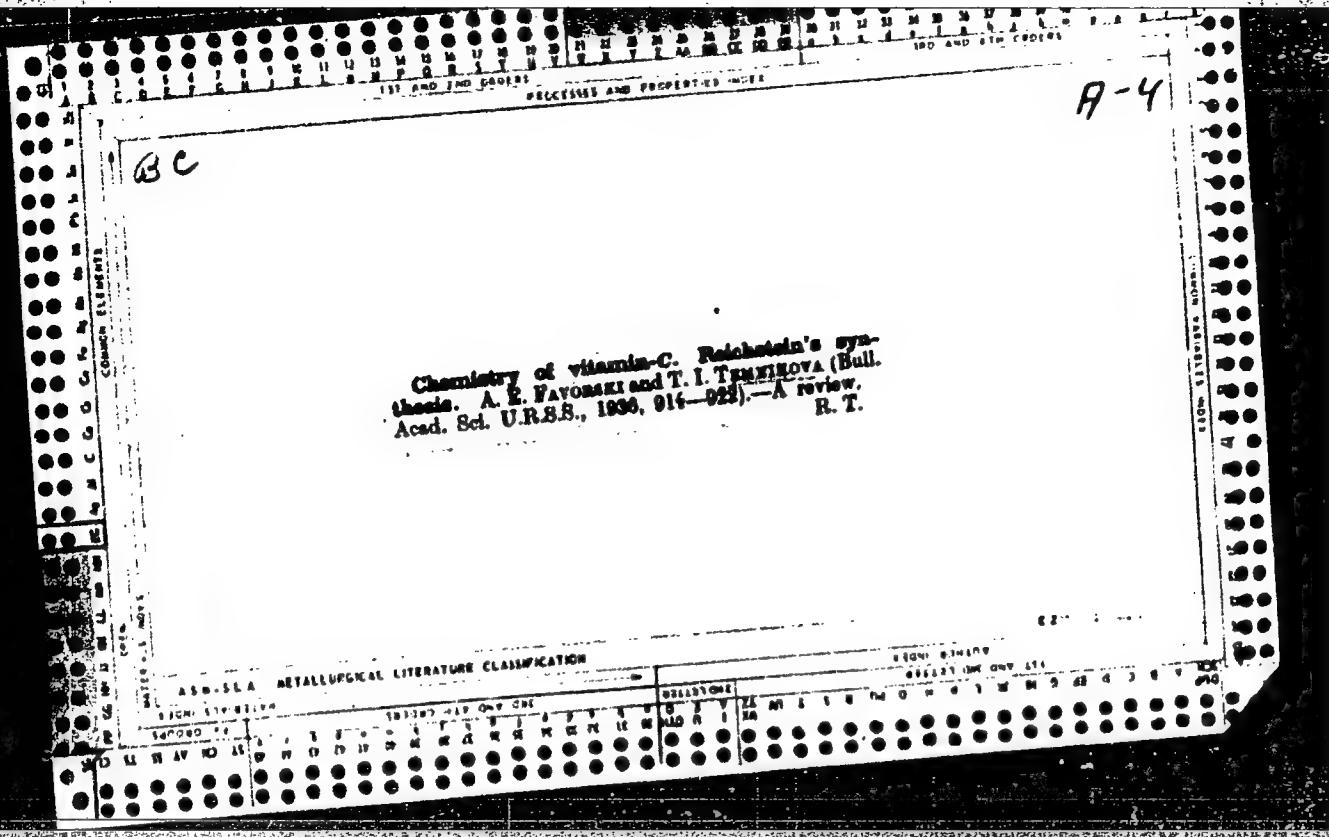
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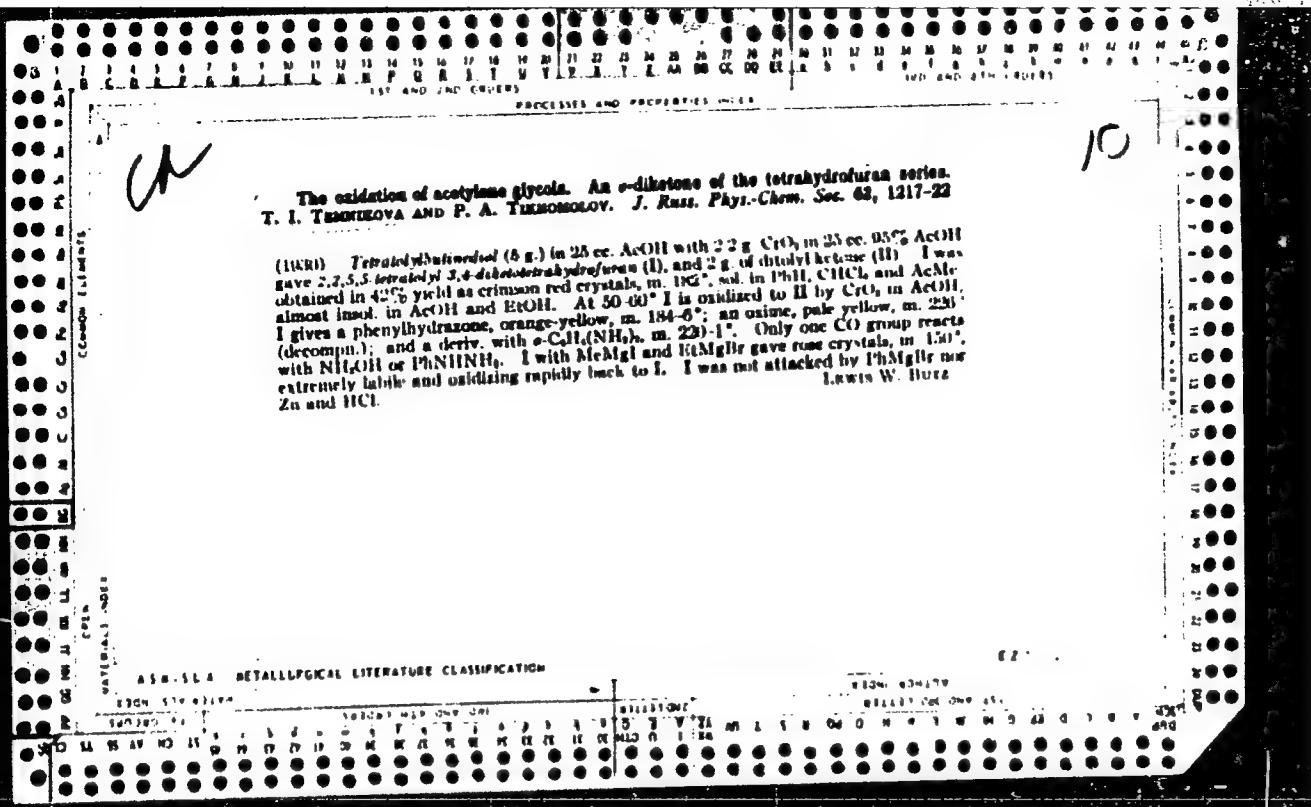
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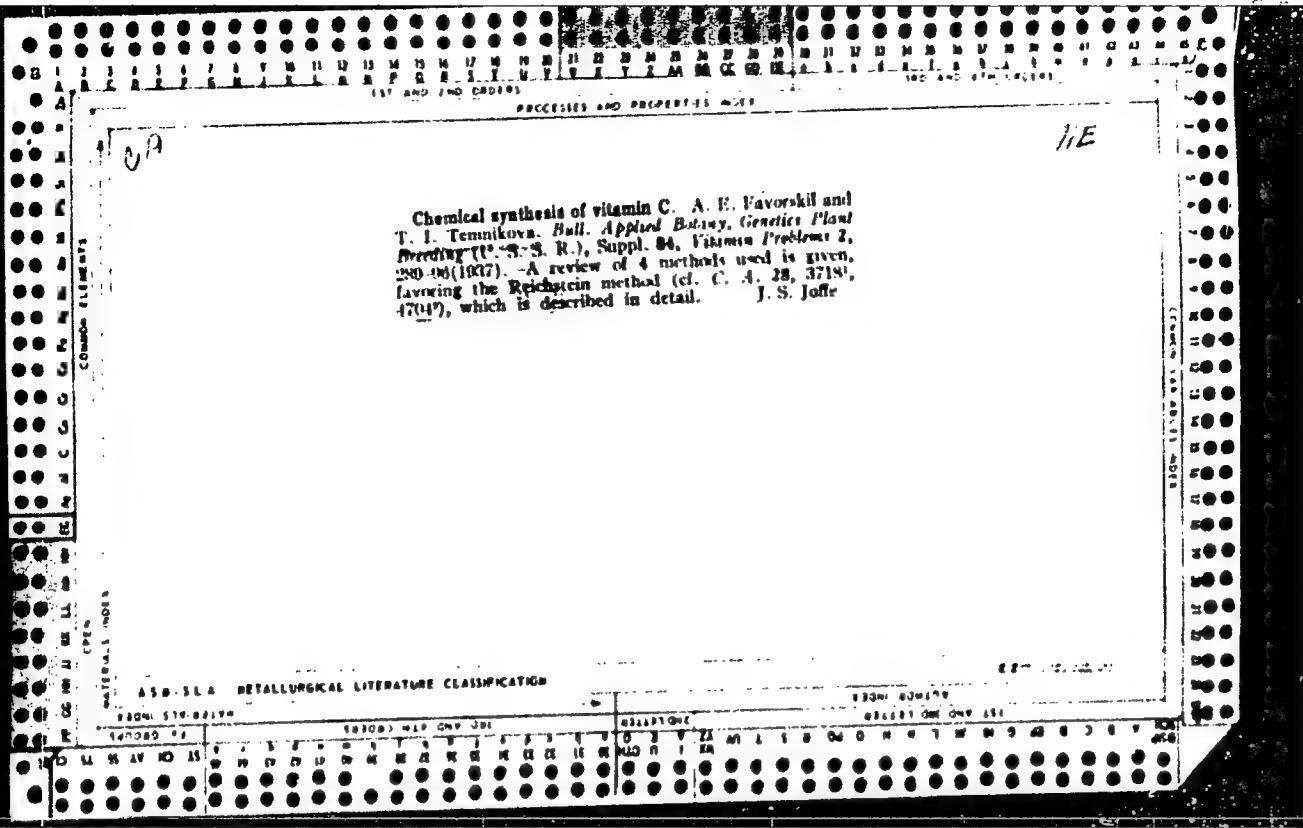
TEMNIKOVA, R. T.

"Experimental Investigations of the Characteristics of Ultrasound Propagation in Suspensions."

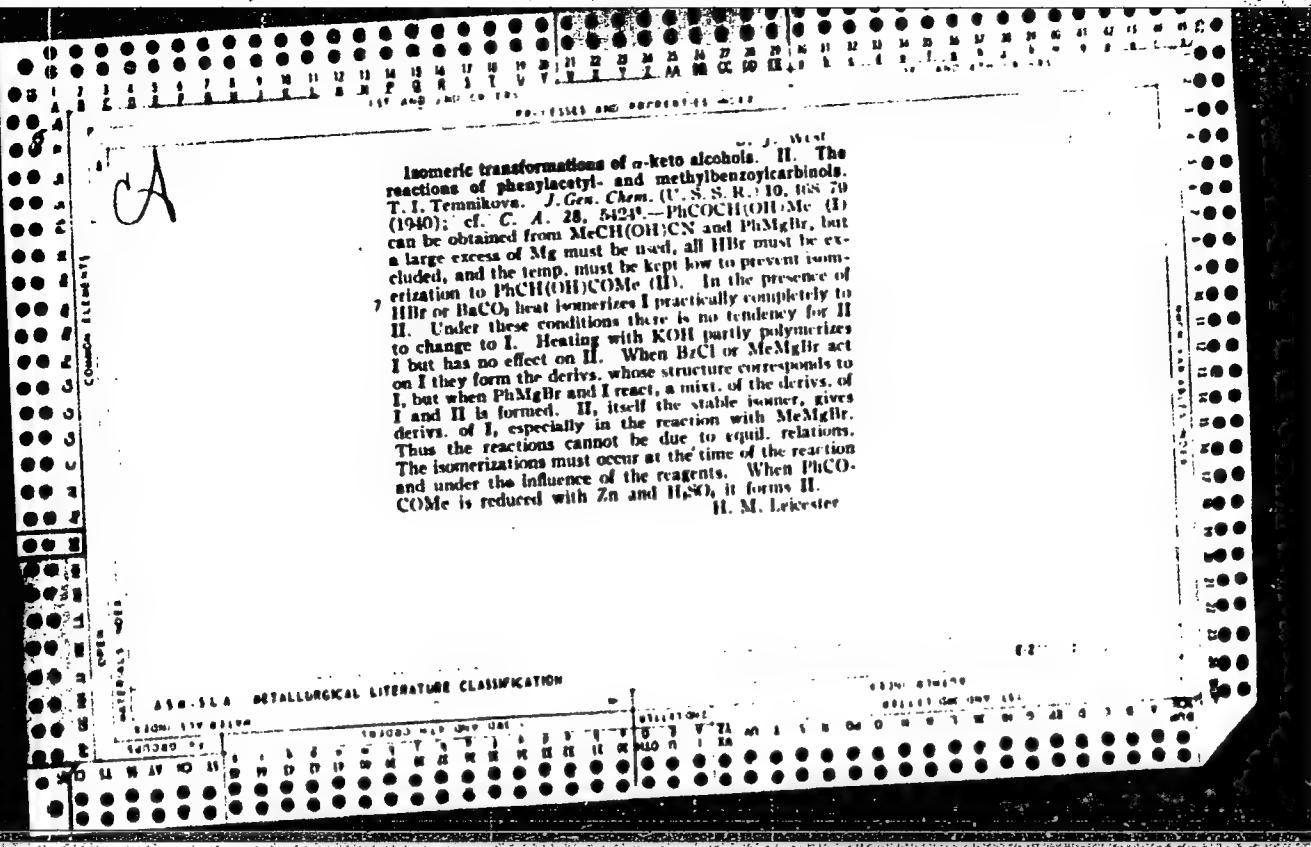
report presented at the 6th Sci. Conference on the Application of Ultrasound in the Investigation of Matter, 3-7 Feb 1958, organized by Min. of Education RSFSR and Moscow Oblast Pedagogic Inst. im N. K. Krupskaya.







ANOMALY OF THE REACTIONS OF  $\alpha$ -BROMO KETONES. T. I.  
Temnikova, J. Russ. Chem. (U. S. S. R.) 8, 1022-8  
(in French, 1029) (1938); cf. C. A. 32, 5424<sup>a</sup>.—The reaction of PhCOCHBrMe with KOBr and KOAc in alc. proceeds normally, giving PhCOCH(OBr)Me, m. 100-101°, and PhCOCH(OAc)Me (*loc. cit.*). The latter with MeMgBr and subsequent reworking gave PhMeC(OH)CH(OH)Me, b.p. 143.5-4.5°. The glycol when oxidized with CrO<sub>3</sub> in aq.  $\text{KHSO}_4$  gave MeCOPh and some *p*-phenylhydrazone. PhCHBrCOMe reacts with KOAc, forming a little of the normal deriv. PhCH(OAc)COMe (I) and chiefly the isomer PhCOCH(OAc)Me (II). If KOBr is used the proportion of the 2 derivs. is reversed. The mixt. of I and II produced with MeMgBr and subsequent treatments MePhC(OH)CH(OH)Me and PhCH(OH)C(OH)Me. Chas. Blanc



Anomalous reactions of  $\alpha$ -bromo ketones. II. Isomerization of 1-bromoethyl methyl ketone. T. I. Lepnikova and V. I. Vekler. *J. Gen. Chem. (U. S. S. R.)* 11, 3-8 (1941); cf. *C. A.* 35, 3777. In continuation of work on the isomerization of  $\alpha$ -bromo ketones, 1-bromoethyl Me ketone (I) was selected as a compd. having a very active Ac grouping. I was prep'd. as follows: Me hexyl ketone (80 g.) dilut. with 1 vol.  $\text{CCl}_4$  was treated, with cooling, with 20 cc. Br in 20 cc.  $\text{CCl}_4$  added dropwise. The product isolated in usual manner amounted to 30 g., bp 93-95°,  $d_4^{20}$  1.2245,  $d_4^{25}$  1.2041,  $d_4^{27}$  1.2077,  $n_d^{20}$  1.45977,  $n_d^{25}$  1.45946; semicarbazone, m. 110-118° (decomp.). A quantity of di-Br ketone was isolated, bp 134-6°,  $d_4^{20}$  1.5405,  $n_d^{20}$  1.5058,  $n_d^{25}$  1.51253,  $n_d^{27}$  1.52197. An acetate was prep'd. by heating I with AcOK in abs.  $\text{EtOH}$  or  $\text{AcOH}$ , the  $\text{EtOH}$  producing a much more rapid reaction. I (25 g.) after esterification in  $\text{AcOH}$  gave 14 g. of acetylaminocarbonyl acetate (II), bp 109-110°,  $d_4^{20}$  0.9519,  $d_4^{25}$  0.9542,  $n_d^{20}$  1.42329,  $n_d^{25}$  1.43325. In order to establish the structure of II it was converted to a glycol by the Grignard reaction, and the glycol oxidized, as follows: 12.7 g. II in  $\text{Et}_2\text{O}$  treated with  $\text{MeMgBr}$  (from 15 g. Mg), after standing overnight and heating for 6 hrs., yielded a small amt. of  $\text{Me}_2\text{COH}$  and 6.5 g. glycol, 2-methyl-3,3-octanediol (III), bp 119-20°,  $d_4^{20}$  0.9347,  $d_4^{25}$  0.9200,  $d_4^{27}$  0.9180,  $n_d^{20}$  1.45590,  $n_d^{25}$  1.45585. III (3.9 g.) was oxidized by mixing with 13 g.  $\text{KHSO}_4$  and 10 cc.  $\text{H}_2\text{O}$  and addn. of 3.25 g.  $\text{CrO}_3$  in 50 cc.  $\text{H}_2\text{O}$  with cooling, followed by steam distil. of the products, which were acetone and caproic acid. The benzoate was prep'd. from I as follows: 20 g. I heated with 25 g.  $\text{BaOK}$  in 100 cc. abs.

$\text{EtOH}$  on a water bath for 4 hrs. gave 16.5 g. acetylaminocarbonyl benzene (IV), bp 146-0.5°,  $d_4^{20}$  1.046,  $d_4^{25}$  1.034,  $n_d^{20}$  1.490,  $n_d^{25}$  1.4895.  $\text{MeMgBr}$  (from 10 g. Mg) treated with 1.12 g. IV in  $\text{Et}_2\text{O}$  gave 1 g.  $\text{Me}_2\text{PhCOH}$ , bp 99°, and 6 g. of a glycol (V), bp 122°.  $\text{MeMgCl}$  treated with IV as above gave, in addition to the above, a small amt. of hydrocarbon m. 49-51°, possibly a dimer of  $\alpha$ -methylstyrene from dehydrogenation of  $\text{Me}_2\text{PhCOH}$ . Oxidation of V, run similar to III, gave  $\text{Me}_2\text{CO}$  and caproic acid as products. The results with both acetylation and benzoylation of I indicate that the reactions in this case are normal, showing that the presence of an Ac grouping does not result in anomalous reaction. G. M. Kosolapoff

*Isomeric transformations of  $\alpha$ -keto alcohols. III.*  
 Reciprocal isomeric transformations of ethylbenzoylcarbinol and phenylpropionylcarbinol. T. I. Temnikova and E. P. Afanaseva. *J. Gen. Chem. (U. S. S. R.)* 11, 70-9(1941); cf. *C. A.* 34, 7879.  
 -Bromination of PhPrCO with Br or PBr<sub>3</sub> in CS<sub>2</sub> or CCl<sub>4</sub> gives 92% PhCOCH(OEt)Et with KOAc in (I), m.p. 146.5-8°, b.p. 153.5-5°. Heated with KOAc in EtOH or AcOH, I gives 70% PhCOCH(OAc)Et, m.p. 154.0°, b.p. 152.3-5°, d<sub>4</sub><sup>20</sup> 1.001, d<sub>4</sub><sup>20</sup> 1.006, n<sub>D</sub><sup>20</sup> 1.59812, n<sub>D</sub><sup>20</sup> 1.52290, M.R. calcd. 153.20, found 156.25, M.R. calcd. 153.30, found 157.07. Upon, with BaCO<sub>3</sub>, gives 70% ethylbenzoylcarbinol (II), b.p. 131.5-2.5°, d<sub>4</sub><sup>20</sup> 1.0827, d<sub>4</sub><sup>20</sup> 1.1000, n<sub>D</sub><sup>20</sup> 1.52033, n<sub>D</sub><sup>20</sup> 1.54448, M.R. calcd. 150.12, found 149.5, M.R. calcd. 147.12, found 147.84. It can also be obtained in 70% yield by heating 12 hrs. on the water bath of I, HCO<sub>3</sub>K and MeOH. The residue in the distn. flask after this reaction, C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>, m.p. 119°, and contg. 2 OH groups. II does not form an oxime, semicarbazone or phenylhydrazone. The phenylketon m.p. 102.3°. When PhCH(OH)COEt (III) is heated with a little H<sub>2</sub>SO<sub>4</sub> in EtOH in a sealed tube, it gives a low-boiling mist. When either II or III in EtOH is allowed to stand at room temp. for 3 hrs. with a little KOH, it gives the same equim. mixt., contg. 60-5% II and 40-35% III. This is proved by the formation of the corresponding glycols with MeMgBr. IV. The reactions of ethylbenzoylcarbinol and phenylpropionylcarbinol with organomagnesium compounds and acid chlorides. T. I. Temnikova. *Ibid.*

77-91--BzCH(OH)Et (I) and MeMgBr give 50% PhMeC(OH)CH(OH)Et, b.p. 148.0-5°. I and EtMgBr give the  $\beta$ -form of PhEtC(OH)CH(OH)Et (II), m.p. 67.8°. With PrMgBr, I give a mixt. contg. chiefly the normal reaction product, PhEtC(OH)CH(OH)Et, and some PhEtC(OH)CH(OH)Ph. PhCH(OH)COEt (III) and MeMgBr give 80% MePhC(OH)CH(OH)Ph, b.p. 162.3°, EtMgBr and III give a mixt. of Et<sub>2</sub>C(OH)CH(OH)Ph (IV), m.p. 98-9°, and a small amt. of II. PrMgBr and III form EtPhC(OH)CH(OH)Ph, m.p. 93.4°. Thus, only the normal glycol is formed in all cases except when the radical in the Grignard reagent is the same as the radical on the CO group in the ketone. This effect is not quite so pronounced as in the Me homologs of these keto alcs. I and BaCl give the normal benzoate, m.p. 17.6-8.5°, and with  $\rho$ -NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COCl, I forms the  $\rho$ -nitrobenzoate, m.p. 62-2.5°. Similarly, III forms only its normal  $\rho$ -nitrobenzoate, m.p. 97-8°; its benzoate is an oil. However, with AcCl, III gives a mixt. of the acetate of III contg. 1.5% of the acetate of I. This is proved by their reaction with EtMgBr to form II and IV and with PrMgBr to form an analogous mixt. In these esters the Mg compd. acts first on the CO group. H. M. Leicester

## ABR-SEA METALLURGICAL LITERATURE CLASSIFICATION

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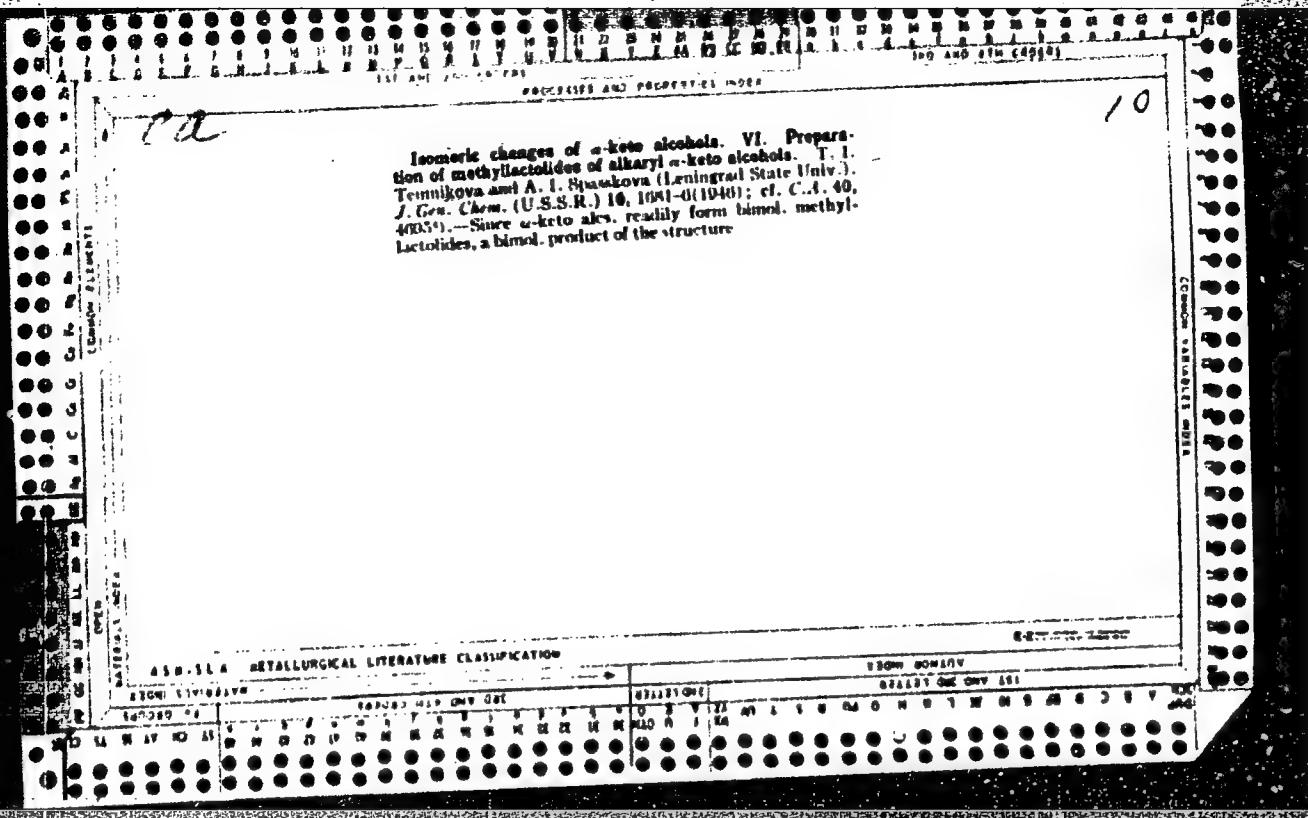
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Keto oxides. I. Hydrogenation of aliphatic and aromatic  $\alpha$ -keto oxides. T. I. Temnikova and V. P. Martynov (Leningrad State Univ.), *J. Gen. Chem.* (U.S.S.R.) 15, 499-513 (1945) (English summary). Chloroacetone (70 g.), 100 g. BaH, and 100 cc. MeOH were treated with cooling and stirring with MeONa (from 16 g. Na) in 230 g. MeOH; after filtration, treatment with water acidified by AcOH, and evap. with Et<sub>2</sub>O, there was obtained 80% *tert*-butyldiglycidic oxide (I), m.p. 134-7°, m. d<sub>4</sub> 7° (from MeOH, then petr. ether); semicarbazone, m. 140-1° (from EtOH). ClCH<sub>2</sub>COR (30 g.) and 35 g. BaH in 10 cc. MeOH, treated as above with MeONa (from 6.3 g. Na) in 80 cc. MeOH, gave 84% 1-phenyl-2-propionylethylene oxide (II), b.p. 138-40°, m.p. 42-3° (from petr. ether), semicarbazone, m. 137-9° (from EtOH). Similarly, MeCOCHClMe gave m.p. 1-phenyl-2-acetylpropylene oxide, b.p. 113-14°, d<sub>4</sub> 1.092, d<sub>4</sub> 1.083, n<sub>D</sub> 1.52186 (III); semicarbazone, m. 115-18° (from EtOH). Hydrogenation of these in Et<sub>2</sub>O in the presence of Pt black was shown to proceed in steps with the addn. of the 1st H<sub>2</sub>; the addn. of H<sub>2</sub> to I and II gave oxides of the 2nd H<sub>2</sub>; the addn. of H<sub>2</sub> to I and II gave oxides of the corresponding unsatd. alcs., while addn. of 2H<sub>2</sub> gave the corresponding glycols. The products thus isolated were: methylpropylcarbinol oxide, b.p. 124-30°, d<sub>4</sub> 1.105, n<sub>D</sub> 1.51233, which, on treatment with water, in the presence of a several drops H<sub>2</sub>SO<sub>4</sub>, hydrated to  $\alpha$ -phenyl- $\omega$ -hydroxyglycerol, m. 95-7° (from Et<sub>2</sub>O); ethylpropylcarbinol oxide, b.p. 132-4°, m. 43-5° (from petr. ether), b.p. 118-19°, d<sub>4</sub> 1.0605, d<sub>2</sub> 1.0722, n<sub>D</sub> 1.51258 (semicarbazone, 158-0° (from EtOH)), which failed to hydrate under the conditions given above. The glycols from the addn. of 2H<sub>2</sub>, were: 1-methyl-2-benzylethylene glycol, m. 152-3°, b.p. 151-5°; 1-ethyl-2-benzylethylene glycol, m. 151-4°; and 1,2-dimethyl-1-benzylethylene glycol, b.p. 100-3°. G. M. Kosolapoff

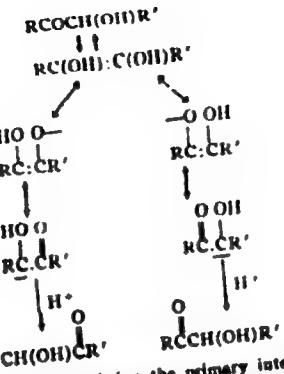
TEMNIKOVA, T. I.

"Investigation in the field of Isomeric Transformations of  $\alpha$ -Keto-alcohols. V. Diphenyl-Acetyl-Carbinol and Dimethyl-Benzoyl-Carbinol." Temnikova, T. I. (p. 514)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1945, Volume 15, no. 6.



CA  
 Isomeric transformations of alkylaryl  $\alpha$ -keto alcohols.  
 T. I. Temnikova. Vestn. Leningrad Univ. 1947, 138-45;  
 cf. C.A. 41, 3220g. Summary of a dissertation without  
 extpl. details. The behavior of several keto alcs. was  
 studied in alk. medium. Ph<sub>2</sub>C(OH)Ac does not isomerize,  
 neither does Me<sub>2</sub>C(OH)Bz. BiCH(OH)Me yields Ph-  
 CH(OH)Ac, PhCOCH(OH)Rt gives an equil. mixt.  
 contg. 40% PhCH(OH)COPh. PhCOCH(OH)COMe  
 gives PhCH(OH)COCH<sub>2</sub>COMe. Neither  $\beta$ -MeOC<sub>2</sub>H<sub>5</sub>  
 COCH(OH)Me nor  $\beta$ -HOCH<sub>2</sub>COCH(OH)Me shows a  
 tendency to isomerize. The mechanism of the isomeriza-  
 tion is portrayed as:



with the same enediol being the primary intermediate,  
 which yields the 2 interchangeable ionic forms. The  $\beta$ -HO  
 or  $\beta$ -MeO derivs. do not isomerize because of the stabilizing  
 influence of resonance between the CO group and the para

Date

substituent. The  $R_2C(OH)$  derivatives do not isomerize because they cannot form enediols. The reactions of keto alcs. with Grignard reagents are summarised as follows:

$\text{PhCOCH}_2(\text{OH})\text{Me}$  and  $\text{MeMgBr}$  give  $\text{PhMeCO}(\text{OH})\text{Me}$ .

$\text{Cl}(\text{OH})\text{Me}$ ,  $\text{PhCH}(\text{OH})\text{COMe}$  and  $\text{MeMgBr}$  give  $\text{PhCH}(\text{OH})\text{COMe}$ .

$\text{PhMeC}(\text{OH})\text{CH}(\text{OH})\text{Me}$  and  $\text{PhCH}(\text{OH})\text{COMe}$  and  $\text{MeMgBr}$  give  $\text{PhMeCO}(\text{OH})\text{CH}(\text{OH})\text{Me}$ .

$\text{PhCOCH}(\text{OH})\text{Me}$  and  $\text{PhCH}(\text{OH})\text{COMe}$  and  $\text{PhMeMgBr}$  give  $\text{PhMeCO}(\text{OH})\text{CH}(\text{OH})\text{Me}$ .

$\text{PhCOCH}_2(\text{OH})\text{Et}$  and  $\text{MeMgBr}$  give  $\text{PhCH}(\text{OH})\text{Et}$ , while  $\text{PhCH}(\text{OH})\text{COMe}$  and  $\text{PhMeMgBr}$  give  $\text{PhCH}(\text{OH})\text{COMe}$ .

$\text{PhCH}(\text{OH})\text{COMe}$  and  $\text{MeMgBr}$  give  $\text{PhCH}(\text{OH})\text{COMe}$ .

$\text{PhCOCH}_2(\text{OH})\text{Et}$  and  $\text{MeMgBr}$  give  $\text{PhCH}(\text{OH})\text{Et}$ , while  $\text{PhCH}(\text{OH})\text{COMe}$  and  $\text{PhMeMgBr}$  give  $\text{PhCH}(\text{OH})\text{COMe}$ .

Five  $\text{PhRC}(\text{OH})\text{CH}(\text{OH})\text{R}$ ,  $\text{PhCOCH}(\text{OH})\text{R}$  and  $\text{MeMgBr}$  give  $\text{PhCH}(\text{OH})\text{CH}(\text{OH})\text{R}$  and  $\text{EtMgBr}$  give  $\text{PhCH}(\text{OH})\text{CH}(\text{OH})\text{R}$ .

$\text{PhCH}(\text{OH})\text{CH}(\text{OH})\text{Et}$  and  $\text{PrMgBr}$  give  $\text{PhCH}(\text{OH})\text{CH}(\text{OH})\text{Et}$  and  $\text{PhMeMgBr}$  give  $\text{PhCH}(\text{OH})\text{CH}(\text{OH})\text{Et}$ .

$\text{PhC}(\text{OH})\text{CH}(\text{OH})\text{Et}$  and  $\text{PhCH}(\text{OH})\text{COMe}$  and  $\text{MeMgBr}$  give  $\text{PhCH}(\text{OH})\text{CH}(\text{OH})\text{Et}$ .

$\text{PhC}(\text{OH})\text{CH}(\text{OH})\text{Et}$  and  $\text{PhMeMgBr}$  give  $\text{PhCH}(\text{OH})\text{CH}(\text{OH})\text{Et}$ .

which is also obtained from  $\text{PhMeMgBr}$  and  $\text{PhCOCH}(\text{OH})\text{Et}$ .

$\text{Me}_2\text{AcCH}(\text{OBz})\text{Et}$  and  $\text{MeMgBr}$  give  $\text{BzCH}(\text{OH})\text{CH}(\text{OH})\text{Et}$ .

by the formation of a coordination complex between the Grignard reagent and the  $\text{CH}(\text{OH})\text{CO}$  group, followed by migration of H between the adjacent C atoms.

Reactions of acyl chlorides with 3 instances with the keto alcs. is explained by the formation of an enediol intermediate only in 3 instances with the keto alcs. given below:

- $\text{PhCOCH}_2(\text{OBz})\text{Me}$  gave  $\text{PhCH}(\text{OBz})\text{COMe}$ .
- $\text{PhCOCH}(\text{OBz})\text{Et}$  and  $\text{PhCH}(\text{OBz})\text{COMe}$  gave  $\text{PhCH}(\text{OBz})\text{COEt}$  and  $\text{BzCl}$ .
- $\text{CO}_2\text{Me}$  and  $\text{AcCl}$  gave  $\text{PhC}(\text{OAc})\text{COMe}$  and  $\text{PhCO}(\text{OAc})\text{COMe}$ .

( $\text{OAc}$ ) $\text{MePh}$ . These isomerizations may be also caused by complex formation with the carbonyl group.

G. M. Kosulipoff

PA 8/49TH4

## USSR / Chemistry - Ketones

Chemistry - Hydrogenation

Apr 48

"Studies in the Field of  $\alpha$ -Keto-oxides: II, Obtaining of and Hydration of Oxides of Tri-Butyl-Styryl-Ketone," T. I. Temnikova, V. A. Kropachev, Chair of State U, 7<sup>th</sup> pp  
"Znur Obshch Khim" Vol XVIII (LXXI), No 4

The cis-and trans- forms of this oxide with melting point 70 - 71 and 80 - 81, respectively, were obtained as two different isomers:  $C_6H_5CHO + (CH_3)_3CCOOC(CH_3)_3 + NaBr + CH_3OH +$  both cases phenyl trimethylacetyl ethylene glycol

## User / Chemistry - Ketones (Contd)

8/49TH4

was obtained by hydration with sulfuric acid. The platinum black, but in the presence of nickel, benzyl trimethyl acetyl carbinol was obtained. Submitted 24 Mar 1947.

Apr 48

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Research in the field of cyclic acetals of hydroxycarbonyl compounds. I. Synthesis and properties of the methyl lactolide of methylbenzoylcarbisole (1-methoxy-1-phenyl-1-propene oxide). T. I. Trannikova and N. N. Kropacheva (Leningrad State Univ.). *J. Gen. Chem. (U.S.S.R.)* 19, No. 10, a383-93(1949)(English translation).—See *C.A.* 44, 1029b.  
E. J. C.

$\beta c$

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*e*-Ketonic esters. III. Selectivity of hydroxylation of benzyl acetone ester (ester) in the presence of phenolene and phenol. I. I. Tsvetkov and V. A. Kropotkin [U. S. Pat. Clas. USSR, 1949, 29, 541—561 (U.S. transl.)]—Hydroxylation of  $^{18}\text{F}$ : Stepany-1-phenoxytan-3-one (benzylacetone oxide) over Pt gives  $^{18}\text{F}$ : 3-

phenylbutan-3-one (benzeneacetone),  
cyclohexylbutan-3-one; with Pd the product is  
**C<sub>17</sub>H<sub>16</sub>O**. The general rule is formulated that if the  
decomposition of esters derived from aliphatic-aromatic un-  
saturated esters or ketones, the *alpha*-keto ring is ruptured at the  
site nearest the *beta* group. Addition reactions of alcohols to  
these compounds are also discussed (no examples given).

opposite  $\text{W}(\text{C}_6\text{H}_5)_3$  and oriented in the same manner. Reduction of  $\text{Pd}(\text{Ph})_4$  in  $\text{CHCl}_3$  yields 1-phenylbenzene-3-one (I) with  $\text{H}_2$  over  $\text{Pd}(\text{Ph})_4$  in  $\text{CHCl}_3$ . Alkalis 1-phenylbenzene-3-one.  $\text{C}_{10}\text{H}_8\text{O}$  ( $100.15$ ),  $m.p.$   $160^\circ$ ;  $\text{IR}$ ,  $\nu = 1685$ ,  $1511$   $\text{cm}^{-1}$ ;  $\text{PMR}$ ,  $\delta = 7.2$ – $7.5$  ( $\text{m}, \text{aromatic}$ ,  $10$  H),  $1.3$  ( $\text{s}, \text{C}_6\text{H}_5\text{CO}$ ,  $3$  H),  $0.9$ – $1.1$  ( $\text{m}, \text{aromatic}$ ,  $5$  H);  $\text{MS}$ ,  $m.p.$   $171$ – $175^\circ$ , which reacts with  $\text{PhLi}$  in  $\text{Et}_2\text{O}$  yields 1-(3-phenylpropenyl)- $\text{C}_6\text{H}_5\text{CO}$ ,  $\text{C}_{13}\text{H}_{10}\text{O}_2$ ,  $m.p.$   $100$ – $102^\circ$ . Oxidation of the latter product with  $\text{CrO}_3$ – $\text{H}_2\text{O}$  gives  $\text{COPh}_2$  and  $\text{BaCO}_3$ . Moderate yields of I are obtained by over  $\text{Pt}$  or  $\text{Pd}$  in  $\text{H}_2$  over  $\text{Pt-Ni}$  leads to  $1 : 2$ -benzene-3,3'-dicarboxylic acid (not isolated). M. DAVIS.

## **METALLURGICAL LITERATURE CLASSIFICATION**

**APPROVED FOR RELEASE: 07/16/2001**

CIA-RDP86-00513R001755220014-4"

USSR/Chemistry - Ketones, Bromo-

Reactions, Anomalous Jul 49

"The Anomalous Reactions of Alpha-Bromo-n-Tolylacetone: III, Research on Alpha-Bromo-n-Tolylacetone (I)", T. I. Temnikova, V. I. Vekler, Chair of Structure of Org. Compounds, Leningrad Ord of Lenin State U imeni A. A. Zhdanov, 6 pp

"Zhur Obshch Khim" Vol XIX, No 7

Chief product of reaction of I with potassium acetate was shown to be acetic ester of n-tolylacetylcarbinol, with only a small part of reaction accompanied by molecular rearrangement with formation of isomeric

USSR/Chemistry - Ketones, Bromo-

Reactions, Anomalous (Contd) Jul 49

ester from methyl-n-tolyl-carbinol. Comparison of these results with those of reaction of potassium acetate with alpha-bromophenylacetone revealed that increased electron density in reaction zone results in a marked increase in reactive capacity of bromine in its interaction with reactive capacity of potassium acetate. Submitted 16 Feb 48.

2/50T54

2/50T54

CH / 9

Isomeric transformations of  $\alpha$ -keto alcohols. VII. Influence of chlorine in the para position on the stability of alkaryl  $\alpha$ -keto alcohols. Methyl(*p*-chlorobenzoyl)carbinol. T. I. Tennikova and R. I. Kulischkova. *Zhur. Obshch. Khim.* (*J. Gen. Chem.*) 19, 1324-34 (1949); cf. *C.A.* 41, 6229y. Slow addn. of 60 g. PhCl and 40 g. Et<sub>2</sub>OOC<sub>2</sub> to 116 g. AlCl<sub>3</sub> in 100 ml. CS<sub>2</sub> and letting stand 2 days, followed by 3 hrs. on a steam bath, gave upon ice treatment 91% *E*-*p*-chlorophenyl ketene, m. 34-6°. This (61.2 g.) in 180 ml. AcOH, treated with 88 g. Br and poured into water, gave 80-90% *1*-bromoethyl *p*-chlorophenyl ketone, m. 77-9° (from ligroin). Heating this (13 g.) with 10 g. KO<sub>2</sub>CH and 35 ml. MeOH in sealed tube 8 hrs. at 128-30° gave 4.3 g. mixed *p*-C<sub>6</sub>H<sub>4</sub>COCH(OH)Me and *p*-C<sub>6</sub>H<sub>4</sub>CH(OH)COMe, b.p. 138-9°, which gave a semicarbazone, m. 183-4° (from EtOH); however, the presence of 2 products is shown by treatment with PhMgBr which gave a glycol mixt., m. 74-81° (from ligroin), apparently *p*-C<sub>6</sub>H<sub>4</sub>CO(OH)PbCH(OH)Me (I) and *p*-C<sub>6</sub>H<sub>4</sub>CH(OH)C(OH)PbMe, since oxidation by Pb(OAc)<sub>4</sub> in AcOH gave *p*-C<sub>6</sub>H<sub>4</sub>COPh, PhAc, AcII, and *p*-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>II. Heating the crude oil from the KO<sub>2</sub>CH-MeOH reaction 30 hrs. with an aq. suspension of BaCO<sub>3</sub> on a steam bath causes isomerization of the keto alk. mixt. to pure methyl(*p*-chlorobenzoyl)carbinol (46% yield), b.p. 180-2°, d<sub>4</sub><sup>20</sup> 1.2365, n<sub>D</sub><sup>20</sup> 1.54738, which yields a semicarbazone, m. 186-8°, while reaction with PhMgBr yields pure I, m. 88.5-9.5°, which with Pb(OAc)<sub>4</sub>, gives only *p*-C<sub>6</sub>H<sub>4</sub>COPh and AcII. A similar isomerization, with poorer yield, takes place on standing 3 days in 1.7% alk. KOH. Refluxing 28 g. *p*-C<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>BrMe with 12 g. KOAc and 50 ml. EtOH 5 hrs. gave 48.5% methyl(*p*-chlorobenzoyl)carbinol acetate, b.p. 135-9°

d<sub>4</sub><sup>20</sup> 1.216, n<sub>D</sub><sup>20</sup> 1.5231, which on treatment with MeMgBr gave *p*-C<sub>6</sub>H<sub>4</sub>CO(OH)MeCH(OH)Me, b.p. 125°, which with Pb(OAc)<sub>4</sub>, gave AcII and *p*-C<sub>6</sub>H<sub>4</sub>COMe (semicarbazone, m. 192-4°, also prep'd. by the Friedel-Crafts method). The use of BiOK instead of KOAc in the above gave the corresponding benzene, m. 92.5° (from ligroin), which is stable to hot aq. BaCO<sub>3</sub> (30 hrs.). The results indicate that the mesomeric effect of the *p*-C<sub>6</sub>H<sub>4</sub> group is greater than that of Me in the intermediate substance formed in the course of isomerization. G. M. Kolosol'off

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**Cyclic acetals of hydroxycarboxyl compounds. I.**  
Preparation and properties of the methyl lactolide of  
methylbenzoylcarbinol (1-methoxy-1-phenyl-1-propene  
oxide). T. I. Temnikova and E. N. Kropacheva (Kafedra  
Stroeniya Org. Soedinenii Leningrad. Gosudarst. Ordona  
Lenina Univ. im. A. A. Zhdanova). Zhur. Obshch. Khim.  
(J. Gen. Chem.) 19, 1917-20 (1949). — PhCOCH(Me)Ph  
(32 g.) in Et<sub>2</sub>O treated slowly with a suspension of MeONa  
(from 10 g. Na) in Et<sub>2</sub>O yielded 10 g. 1-methoxy-1-phenyl-  
1-propene oxide, Ph(MeO)C<sub>2</sub>CHMe<sub>2</sub>, b<sub>4</sub> 63.5°, d<sub>4</sub><sup>20</sup>

1.0521, n<sub>D</sub><sup>20</sup> 1.40604, which polymerizes on standing (mol. wt. doubles in 24 hrs.). The product (0.5 g.) treated with 1.5 g. PhNHNNH<sub>2</sub> in EtOH contg. a little AcOH, heated 0.5 hr. on a steam bath, and let stand overnight gave 0.45 g. PAC(=NNHPb)CHMeNNHNPb, m. 120° (from EtOH). Heating the oxide with H<sub>2</sub>SO<sub>4</sub> in all dilns. gave mostly tar; with 5% H<sub>2</sub>SO<sub>4</sub> there was obtained a very low yield of a solid, m. 208° (C<sub>11</sub>H<sub>10</sub>O<sub>4</sub>), and phenylacetylcarmolin, b<sub>4</sub> 120-1° (semicarbazone, m. 180°). Addn. of the oxide (8.5 g.) to 5% H<sub>2</sub>SO<sub>4</sub> preheated to 80° and stirring 1.5 hrs. on a steam bath gave 3.43 g. methylbenzoylcarmolin, b<sub>4</sub> 63.5°, n<sub>D</sub><sup>20</sup> 1.54571 (forms a semicarbazide, m. 230°, on prolonged standing with the reagent). Reaction of this hydrolysis product with PhMgBr gave 1,1-diphenyl-1,2-propanediol, m. 91-2° (from petr. ether), which gives Pb<sub>2</sub>CO on chromic acid oxidation. Addn. of 3 ml. 3% MeOH-HCl to 0.5 g. oxide gave, after vigorous action, 0.3 g. 2,2-dimethyl-2,5-dimethyl-3,5-diphenyl-9-dioxane, m. 251° (from CdI<sub>4</sub>). The nomenclature of olefin oxides and lactols is discussed; the use of the prefix cyclo for the ring forms is urged.

*α*-Keto oxides. III. Selectivity of hydrogenation of benzylideneacetone oxide in the presence of platinum and palladium. T. I. Temnikova and V. A. Kropachev (Leningrad State Univ.), *Zhur. Obshch. Khim.* (J. Gen. Chem.) 19, 2060-81 (1949); cf. *C.A.* 43, 139c. Hydrogenation of benzylideneacetone oxide in EtOH or Et<sub>2</sub>O with Ni-Pd at room temp. yields 80% *PtCH<sub>2</sub>CH(OH)Ac*, b.p. 90°, d<sub>4</sub><sup>20</sup> 1.0853, m.p. 1.52403; semicarbazone, m. 100-70° (from EtOH); phenylosazone, m. 171-3° (from EtOH). Treatment of the keto alc. with PhMgBr gave *PtCH<sub>2</sub>CH(OH)C(OH)MePh*, m. 108.5-0.5° (from *c*-roin). Hydrogenation of the oxide over Ni-Pt yields *O.CIPh.CHCH(OH)Me* described earlier (*C.A.* 40, 46044). Arguments are presented for classifying the addition of alc. to olefin oxides as nucleophilic reactions which may be modified by preliminary deformation of the oxide ring by acids. G. M. Kosolapoff

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*Cyclic acetals of hydroxycarbonyl compounds II*

Action of alkali on 1-methoxy-1-phenyl-1-propene oxide  
E. I. Temnikova and R. N. Kropacheva (Leningrad State  
Univ.), Zhur. Obshchey Khim., (J. Gen. Chem.) 21, 183-6  
(1951); cf. C.A. 44, 6402d. Heating 7 g. 1,2-epoxy-1-  
methoxy-1-phenylpropane with 100 ml. 10%  $K_2CO_3$ , 1.3  
hrs. gave 3.27 g. oil, b.p. 104°, 0.2°/1.03, w.t. 1.312; identified  
as  $P(CH(OH)Ac)_2$ ; semicarbazone, m. 192-3°; reaction  
with  $PhMgBr$  gave 1,2-diphenyl-1,2-propanediol, m. 95-0°.  
Possibly the hydrolysis of the oxide first yields  $PhCH(OH)_2$ ,  
Me, which then isomerizes into the more stable final product.  
Not a trace of org. acid forms in the hydrolysis. The bearing  
of the result on the possible mechanism of hydrolysis of  
 $\alpha$ -Br ketones is discussed. G. M. Kiselevoff

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*a*-Keto oxides. IV. Hydrogenation of *a*-keto oxides as a method of preparation of *a*-keto alcohols. I. J. Linnikova and V. A. Krapachev (A. A. Zhdanov State Univ., Leningrad). *Zhur Obshchel Khim.* (J. Gen. Chem.) 21, 201-8 (1951); cf. *C.A.* 44, 7271. The previously proposed hydrogenation of *a*-keto oxides over Pt-Ni is a generally applicable method for addn. of 2 H, after which the reaction stops. Almost no addn. of H occurs with iso-Pt-styryl ketone oxide over Pt black. Addn. of 14.5 g. iso-PtCO<sub>2</sub> to CH<sub>2</sub>Ni in RbOH, followed by passage of HBr at 0°, gave 74% *bromomethyltin-Pt-ketone*, m. 84-6°, nD<sup>25</sup> 1.4078. This (15.7 g.) and 13 g. BaH in 10 ml. MeOH slowly treated at 5° with 2.15 g. Na in 80 ml. MeOH, stirred 1 hr., and treated with dil. AcOH, gave 65% iso-Pt-styryl keto-alkide, C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>, b. 110.5-115.5°, d<sub>25</sub><sup>20</sup> 1.055, nD<sup>25</sup> 1.5100 (liberates iodine from AcOH-KI; does not yield CH<sub>4</sub> with MeMgI; reduces Pechling salt, only on heating); *semicarbazone*, m. 77-80° (from MeOH), 137-40° (on rapid heating in sealed tube) (from RbOH). Hydrogenation over Pt black did not proceed at normal conditions. Hydrogenation over Pd-Ni catalyst (by reduction of PdCl<sub>4</sub>·2NaCl and Ni; cf. previous papers) gave the keto alc., *PtCH<sub>2</sub>CH(OH)COCH<sub>3</sub>*, CH<sub>2</sub>O<sub>2</sub>, b. 125°, d<sub>25</sub><sup>20</sup> 1.055, nD<sup>25</sup> 1.5100; *semicarbazone*, m. 136.5-138° (from dil. MeOH); neither the *p*-nitrophenyl-hydrazone nor osazone could be made. The keto alc. (1.85 g.) with MeMgBr readily gave 80% 2,3-dimethyl-5-phenyl-3,4-pentadienol, needles, m. 101.5-2.5° (from petr. ether), which on oxidation with Pb(OAc)<sub>4</sub> gave iso-PrCOMe, and BaOH. Similar hydrogenation of Et styryl ketone oxide gave 78-84% *benzylpropionylcarbonyl*, b. 110-10.5°, d<sub>25</sub><sup>20</sup> 1.0810, nD<sup>25</sup> 1.51630 (*semicarbazone*, m. 140-9.5° (from RbOH)), which with PhMgBr gave 70% 1,3-diphenyl-2,3-pentadienol, m. 83.5-4.5°, yielding R(COPh) and BaOH with Pb(OAc)<sub>4</sub>. G. M. Kusolapoff

Chem A

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**Isomeric transformations of  $\alpha$ -keto alcohols VIII.**  
**Effect of a methyl group in the para position in a phenyl nucleus on the relative stability of isomeric alkaryl  $\alpha$ -keto alcohols.** T. I. Temnikova and L. A. Petrova (Leningrad State Univ.), Zhur. Obshch. Khim. (J. Gen. Chem.) 21, 677-81 (1951), cf. C. I. 44, 1056d, 1112f. Introduction of Me into the para position of Ph in alkaryl  $\alpha$ -keto alcohols changes the properties of the substances by the inductive and mesomeric effects of the Me group. Of  $\text{Me}_2\text{CHCOCH}_2\text{Ph}$  and  $\text{MeCH}_2\text{CHOHCOCMe}$ , the former is most stable. A solid soln. of 30 g.  $\text{HCOOK}$  in  $\text{MeOH}$  at  $40^\circ$  is treated with a 50%  $\text{MeOH}$  soln. of  $\rho$ - $\text{MeCH}_2\text{CHBrAc}$  (31 g.  $\rho$ - $\text{MeCH}_2\text{CH}_2\text{Br}$ ) brominated, and the crude product used directly (and stirred at gentle reflux 10 hrs. to yield 27% of  $\rho$ -*isobromocrotonic acid* (I, *a*, b, 103-1%, *b*,  $mp$ , 123-0%), which on standing rapidly deposits a solid residue, *semicarbazone*, *mp*, 180-91° (from EtOH); *oxime*, *mp*, 141-3° (from EtOH). Treatment of the *alb.* with 2-3%  $\text{MeOH-HCl}$  yields the *cyclotriphosphazide*, *CuHsP*, *mp*, 255°. Attempts to burn the carbonyl by heating the Br ketone in a sealed tube

with  $\text{HCOOK}$  at  $140^\circ$  gave 10% *isobutyronitrile*, *mp*, 106-107° (isolated as the *oxime*, *mp*, 122-3°) decomposed in a sealed tube). The solid *mp*, 173°, formed on storage of the carbonyl, has no OH groups, nor does it form a semicarbazone, possibly it is  $\beta$ - $\text{MeCH}_2\text{CH}_2\text{COO}$ . Heating  $\rho$ - $\text{MeCH}_2\text{CH}_2\text{COCH}_2\text{BrMe}$  with  $\text{HCOOK}$  and  $\text{MeOH}$  in a sealed tube for two at  $140^\circ$  gave 37% product (II), *mp*, 129-31°, *bc*, 100-105°, semicarbazone, *mp*, 188-91°, does not depress the *mp.* of *I* semicarbazone; the yield of the semicarbazone indicates that the condensation yields *enantiomers* of keto acids (contg. some 20-30% I). Treatment of the crude II with  $\text{H}_2\text{NCONHNH}_2$  in  $\text{aq. MeOH}$ , filtration of the product, semicarbazone, acidification of the filtrate with  $5\%$   $\text{H}_2\text{SO}_4$ , warming on a steam bath, and evg. with  $\text{Et}_2\text{O}$  gave 66% *trimesic acid* (cyclotriphosphazide), *mp*, 230-231° (from  $\text{CH}_2\text{Cl}_2$ ). Heating  $\text{BrCl}$  with crude II and  $\text{BaCl}_2$  failed to yield a Br deriv., but heating 4 g.  $\beta$ - $\text{MeCH}_2\text{CH}_2\text{COCH}_2\text{BrMe}$  and 4.2 g.  $\text{BrOK}$  in  $\text{EtOH}$  readily gave *methylenecyclo-*  
*hexa-2,4-dienoate*, *mp*, 96-97° (from EtOH). The isomerization of the 2-ketones was followed by thermal analyses of their lactolides. Crude II, on this basis contains 20-35% I and 75-80%  $\rho$ - $\text{MeCH}_2\text{CH}_2\text{COCH}_2\text{OH Me}$  (III). Heating this mixt. (cf. Fig. 3) 20 hrs. to  $100^\circ$  with fresh  $\text{BaCO}_3$  in a  $\text{CO}_2$  stream give the cyclolactide, *mp*, 226°, correspondingly to 90-95% III. Heating substantially pure I under similar conditions give a cyclolactide whose *mp*, 227°, indicated 23-25% III content. The cyclolactide binary system has a *mp*, *mp*, at about 210°, at approx. 10% I content. The pure *enantiomeric* keto acids could not be isolated. G. M. K.

1951

USSR/Chemistry - Acetylene Derivatives Oct 51

"Action of Aluminum Amalgams on 3-Chloro-3-Methylbutyne-1," T. I. Temnikova, Z. A. Baskova, Chair of Structure of Org Compds, Leningrad State U imeni A. A. Zhdanov

"Zhur Obshch Khim" Vol XXI, No 10, pp 1823-1825

Reduction of 3-chloro-3-methylbutyne-1 with Al amalgam in boiling aq Et alc yields mixt of hydrocarbons: isopropylacetylene (~ 30%), iso-propenylacetylene (~ 60%), and nonsym dimethylallene (~ 10%).

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Molecular rearrangements of  $\alpha$ -keto alcohols. IX.  
Reaction of methyl  $\beta$ -tolyl ketals with organomagnesium compounds. T. I. Semenikova and L. A. Petrova (A. A. Zhdanov State Univ., Leningrad). Zhur. Obshch. Khim. (J. Gen. Chem.) 21, 1877-83 (1951); cf. C.A. 45, 9304b. Reactions of  $\text{McMgBr}$  with  $p\text{-MeC}_6\text{H}_4\text{COCH}(\text{OH})\text{Me}$  (I) and  $p\text{-MeC}_6\text{H}_4\text{CH}(\text{OH})\text{Ac}$  (II) lead to considerable enolization of the latter substances. Introduction of a  $p\text{-Me}$  group thus enhances enolization and raises the yield of "abnormal" reaction products (loc. cit.). To  $\text{McMgBr}$  (from 11.6 g.  $\text{MeBr}$ ) in  $\text{Et}_2\text{O}$  was added 4.9 g. I with ice cooling and the mixt. let stand 12 hrs., refluxed 4 hrs., and worked up as usual, yielding 49.4%  $p\text{-MeC}_6\text{H}_4\text{CM}(\text{OH})\text{CH}(\text{OH})\text{Me}$ , b.p. 160-161° m. 84-8° which with  $\text{CrO}_3\text{-H}_2\text{O}$  at 80° gave AcI and  $p\text{-AcC}_6\text{H}_4\text{Me}$ . I (8 g.) with  $\text{PhMgBr}$  (from 19 g.  $\text{PhBr}$ ) similarly gave 20%  $l\text{-phenyl-1-}p\text{-tolyl-1,2-propanediol}$ , m. 84-8°, which with  $\text{Pb(OAc)}_2\text{-AcOH}$  gave AcI and  $p\text{-BuCrH}_3\text{Me-p}$ . II (8 g.) with  $\text{EtMgBr}$  yielded 1.7 g. oily product, b.p. 145-9°, oxidized to AcI,  $\text{MeEtCO}$ ,  $p\text{-MeC}_6\text{H}_4\text{COEt}$ , and  $p\text{-MeC}_6\text{H}_4\text{CO}_2\text{H}$ , thus showing that a mixt. of glycols formed; about 33%  $3\text{-}p\text{-tolyl-3,3-propanediol}$  and 67%  $l\text{-}p\text{-tolyl-2-methyl-1,2-butanediol}$ . Similarly II with  $\text{PhMgBr}$  gave a mixt. of glycols, m. 87-8°, oxidized to AcI,  $p\text{-BrCrH}_3\text{Me}$ , AcPh, and  $p\text{-MeC}_6\text{H}_4\text{CO}_2\text{H}$ , from the relative amts. of the glycol mixt. was shown to be 88%  $l\text{-}p\text{-tolyl-2-phenyl-1,2-propanediol}$  and 15%  $l\text{-phenyl-1-}p\text{-tolyl-1,2-propanediol}$ . The reaction proceeds by a 1st-step reaction of  $\text{RMgX}$  with the OH of the carbinol, followed by development of the pos. pole at the carbonyl C with addn. of  $\text{MgBr}$  to carbonyl the O, the subsequent course being detd. by the structure of the carbinol.

G. M. Kosolapoff

CTRSP<sup>L</sup> Vol. 5-No. 1

Jan. 1952

Zemskova, I.A. and Kropacheva, E.N. (A.E. Favorski Laboratory, A.A. Zhdanov Leningrad  
State University). Transformations of methyl lactolide of methyl benzoylcarbamid (oxy-<sup>18</sup>-  
methylene phenylpropylene) in an acid medium. 291-4

Akademiya Nauk, S.S.R., Doklady Vol. 78, No. 2, 1951

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4

GTRSPN No. 45

Ternakova, I.I. and Tikhomolova, M.P. (Ural State University). The  
structure of Butlerov's oxoetene  $(\text{CH}_3)_2\text{C}=\text{C}(\text{O})\text{C}(\text{H}_3)_2$ . 613-6

Akademiya Nauk S.S.R., Doklady Vol. 79 No. 4, 1951

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4"

1. TEMNIKOVA, T. I.
2. USSR (600)
4. Chemistry, Organic
7. Molecular rearrangement, tautomeric and isomeric conversion. Part 1. Development of principle ideas in the works of A. M. Butlerov, Vest. Len. Univ., 7, No. 2, 1952 .
9. Monthly List of Russian Accessions, Library of Congress, February 1953. Unclassified.

TEMNIKOVA, T. I.

Temnikova, T. I., Kropachev, V. A.- "Investigation of isomeric transformations of -keto alcohols. IX. Investigation of benzylacetylcarbinol." (p. 813)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1952, Vol. 22, No. 5

TEMNIKOVA, T.I.

Chemical Abst.  
Vol. 48 No. 5  
Mar. 10, 1954  
Organic Chemistry

Isomeric transformations of  $\alpha$ -oxo alcohols. X. ~~Acetyl-~~  
~~acrylic alcohol~~. T. I. Temnikova and V. A. Kropachev  
(A. A. Zhdanov State Univ., Leningrad). J. Gen. Chem.  
U.S.S.R. 22, 875-7 (1952) (Engl. translation).—See C.A.  
47, 3208e. H. L. H.

MR  
7-26-54

TEENIKOVA, T. I., KULACHKOVA-KMITO, Ye. I.

Alcohols.

Molecular rearrangements of -keto alcohols. Part. II. Molecular rearrangements of esters of -keto alcohols during methanolysis. Zhur. ob.khim. 22 No. 3, 1952.

9. Monthly List of Russian Accessions, Library of Congress, November 1952, Unc1.

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4"

TEMNIKOVA, T. I.

Chemical Abst.  
Vol. 48 No. 5  
Mar. 10, 1954  
Organic Chemistry

Molecular rearrangements of  $\alpha$ -oxo alcohols. XI.  
Molecular rearrangements in methanolysis of esters of  $\alpha$ -  
oxo alcohols. T. I. Temnikova and E. I. Kulachkova-  
Kmito (Zhdanov Leningrad State Univ.). J. Gen. Chem.  
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47, 4857d. H. L. H.

(3)

MA  
1-28-52

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4

TEMNIKOV, T I

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APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4"

TEMNIKOVA, T. I., BASKOVA, Z. A. and KHAIMOVA, M. A.

On the Addition of Iodine Chloride to  $\alpha,\beta$ -Diphenylpropylene and  
 $\alpha,\beta$ -Diphenylethylene, page 874, Sbornik statey po obshchey khimii  
(Collection of Papers on General Chemistry), Vol II, Moscow-Leningrad,  
1953, pages 1680-1686.

Chair of the Structure of Organic Compounds, Leningrad State U

VOL 21 NO 1

Cyclic acetals of hydroxycarboxylic compounds. IV  
Methyl lactide of dimethylbenzoate and its trimers  
formations. T. I. Terminata and S. I. Almoldi (A. A.  
Zhdanov, Sov. Chem. Technol.) Zhur. Organich. Khim.  
23, 1338-147 (1967); C.A. 68, 2054a. To 20 g of 10%  
NaOH in 200 ml H<sub>2</sub>O was added slowly 70 g BeCl<sub>2</sub>·6H<sub>2</sub>O,  
and after 7-10 hrs. the filtrate gave dimethylbenzoate by  
distillation.

*Me lactide*, PhCO(Me)<sub>2</sub>CH<sub>2</sub>O(Me) (I). b.p. 35-55°, n<sub>D</sub>  
1.5524, d<sub>4</sub> 1.0124, m.p. 140.2-141.1°, 1.49543, n<sub>D</sub> 1.55033  
I with one mol H<sub>2</sub>NOH·H<sub>2</sub>O and AgCl gave dimethylbenzoic  
carboxylic anhydride II, M.P. 140-141°, with 2.4  
(O<sub>2</sub>N<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub> in aq. meth. with a trace of H<sub>2</sub>O,  
gave dimethylbenzoic acid III, a cyclic anhydride, b.p. 110-115°.  
The same reaction with 2 mol NaOH gave BeCl<sub>2</sub>·6H<sub>2</sub>O.  
I reacts with 1 mol NaOH to give PhCO(Me)<sub>2</sub>CH<sub>2</sub>O(Me)<sub>2</sub>  
and 1 mol H<sub>2</sub>CO<sub>2</sub>. The latter is a colorless oil which  
on which you add 1 mol PhCO(Me)<sub>2</sub> and a substituent in  
1 mol or greater. It has its absorption spectrum resembling  
that of the cyclohexanehydrochloride of PhCO(Me)<sub>2</sub>  
(cf. J. Org., 27, 1962). The product is the same if one is  
replaced by another. The yield of the anhydride is 24  
hrs. at 100°, 100% yield. The anhydride is a white  
solid, M.P. 140-141°, [α]<sub>D</sub> -10.5°, m.p. 140.2-141.1°,  
d<sub>4</sub> 1.0124, m.p. 140.2-141.1°, 1.49543, n<sub>D</sub> 1.55033.  
BeCl<sub>2</sub>·6H<sub>2</sub>O and precipitate in 2 mol NaOH reacted  
gave after 5 hrs. an isolated yield of the anhydride in about  
1.4% yield. M.P. 140.2-141.1°, 1.49543, where  
decomposition is noted. The anhydride has 17.2% carbonyl  
mass of a CO group; IR no max at 3200 cm<sup>-1</sup>. The oxidative

and NaOH in THF. V. Methyl lactides of ester



benzoylcarbinol and methyl *p*-nitrophenylcarbinol

IV. To 1 g MeCl<sub>2</sub> suspended in 10 ml H<sub>2</sub>O was added 0.5 g MeCl<sub>2</sub>·6H<sub>2</sub>O, the most filtered after 2 hrs. at

room temp. and the filtrate dried, giving 1 g PhCO(Me)<sub>2</sub>.

PhCO(Me)<sub>2</sub>·6H<sub>2</sub>O (I) was dissolved in 10 ml H<sub>2</sub>O and 1.5 g NaOH was added, giving the 1,4-dimethoxy-2-methyl-3,5-dihydro-1H-1,3-dioxole-2,5-dione (II), M.P. 140-141°, 1.49543, n<sub>D</sub> 1.55033. IR: 3030, 1730, 1680, 1650, 1580, 1550, 1450, 1350, 1250, 1150, 1050, 950, 850, 750, 650 cm<sup>-1</sup>. The IR spectrum is similar to that of the anhydride of PhCO(Me)<sub>2</sub> (cf. J. Org., 27, 1962). The IR spectrum of II is similar to that of the anhydride of PhCO(Me)<sub>2</sub> (cf. J. Org., 27, 1962).

IR: 3030, 1730, 1680, 1650, 1580, 1550, 1450, 1350, 1250, 1150, 1050, 950, 850, 750, 650 cm<sup>-1</sup>.

UV: 200, 205, 210, 215, 220, 225, 230, 235, 240, 245, 250, 255, 260, 265, 270, 275, 280, 285, 290, 295, 300, 305, 310, 315, 320, 325, 330, 335, 340, 345, 350, 355, 360, 365, 370, 375, 380, 385, 390, 395, 400, 405, 410, 415, 420, 425, 430, 435, 440, 445, 450, 455, 460, 465, 470, 475, 480, 485, 490, 495, 500, 505, 510, 515, 520, 525, 530, 535, 540, 545, 550, 555, 560, 565, 570, 575, 580, 585, 590, 595, 600, 605, 610, 615, 620, 625, 630, 635, 640, 645, 650, 655, 660, 665, 670, 675, 680, 685, 690, 695, 700, 705, 710, 715, 720, 725, 730, 735, 740, 745, 750, 755, 760, 765, 770, 775, 780, 785, 790, 795, 800, 805, 810, 815, 820, 825, 830, 835, 840, 845, 850, 855, 860, 865, 870, 875, 880, 885, 890, 895, 900, 905, 910, 915, 920, 925, 930, 935, 940, 945, 950, 955, 960, 965, 970, 975, 980, 985, 990, 995, 1000, 1005, 1010, 1015, 1020, 1025, 1030, 1035, 1040, 1045, 1050, 1055, 1060, 1065, 1070, 1075, 1080, 1085, 1090, 1095, 1100, 1105, 1110, 1115, 1120, 1125, 1130, 1135, 1140, 1145, 1150, 1155, 1160, 1165, 1170, 1175, 1180, 1185, 1190, 1195, 1200, 1205, 1210, 1215, 1220, 1225, 1230, 1235, 1240, 1245, 1250, 1255, 1260, 1265, 1270, 1275, 1280, 1285, 1290, 1295, 1300, 1305, 1310, 1315, 1320, 1325, 1330, 1335, 1340, 1345, 1350, 1355, 1360, 1365, 1370, 1375, 1380, 1385, 1390, 1395, 1400, 1405, 1410, 1415, 1420, 1425, 1430, 1435, 1440, 1445, 1450, 1455, 1460, 1465, 1470, 1475, 1480, 1485, 1490, 1495, 1500, 1505, 1510, 1515, 1520, 1525, 1530, 1535, 1540, 1545, 1550, 1555, 1560, 1565, 1570, 1575, 1580, 1585, 1590, 1595, 1600, 1605, 1610, 1615, 1620, 1625, 1630, 1635, 1640, 1645, 1650, 1655, 1660, 1665, 1670, 1675, 1680, 1685, 1690, 1695, 1700, 1705, 1710, 1715, 1720, 1725, 1730, 1735, 1740, 1745, 1750, 1755, 1760, 1765, 1770, 1775, 1780, 1785, 1790, 1795, 1800, 1805, 1810, 1815, 1820, 1825, 1830, 1835, 1840, 1845, 1850, 1855, 1860, 1865, 1870, 1875, 1880, 1885, 1890, 1895, 1900, 1905, 1910, 1915, 1920, 1925, 1930, 1935, 1940, 1945, 1950, 1955, 1960, 1965, 1970, 1975, 1980, 1985, 1990, 1995, 2000, 2005, 2010, 2015, 2020, 2025, 2030, 2035, 2040, 2045, 2050, 2055, 2060, 2065, 2070, 2075, 2080, 2085, 2090, 2095, 2100, 2105, 2110, 2115, 2120, 2125, 2130, 2135, 2140, 2145, 2150, 2155, 2160, 2165, 2170, 2175, 2180, 2185, 2190, 2195, 2200, 2205, 2210, 2215, 2220, 2225, 2230, 2235, 2240, 2245, 2250, 2255, 2260, 2265, 2270, 2275, 2280, 2285, 2290, 2295, 2300, 2305, 2310, 2315, 2320, 2325, 2330, 2335, 2340, 2345, 2350, 2355, 2360, 2365, 2370, 2375, 2380, 2385, 2390, 2395, 2400, 2405, 2410, 2415, 2420, 2425, 2430, 2435, 2440, 2445, 2450, 2455, 2460, 2465, 2470, 2475, 2480, 2485, 2490, 2495, 2500, 2505, 2510, 2515, 2520, 2525, 2530, 2535, 2540, 2545, 2550, 2555, 2560, 2565, 2570, 2575, 2580, 2585, 2590, 2595, 2600, 2605, 2610, 2615, 2620, 2625, 2630, 2635, 2640, 2645, 2650, 2655, 2660, 2665, 2670, 2675, 2680, 2685, 2690, 2695, 2700, 2705, 2710, 2715, 2720, 2725, 2730, 2735, 2740, 2745, 2750, 2755, 2760, 2765, 2770, 2775, 2780, 2785, 2790, 2795, 2800, 2805, 2810, 2815, 2820, 2825, 2830, 2835, 2840, 2845, 2850, 2855, 2860, 2865, 2870, 2875, 2880, 2885, 2890, 2895, 2900, 2905, 2910, 2915, 2920, 2925, 2930, 2935, 2940, 2945, 2950, 2955, 2960, 2965, 2970, 2975, 2980, 2985, 2990, 2995, 3000, 3005, 3010, 3015, 3020, 3025, 3030, 3035, 3040, 3045, 3050, 3055, 3060, 3065, 3070, 3075, 3080, 3085, 3090, 3095, 3100, 3105, 3110, 3115, 3120, 3125, 3130, 3135, 3140, 3145, 3150, 3155, 3160, 3165, 3170, 3175, 3180, 3185, 3190, 3195, 3200, 3205, 3210, 3215, 3220, 3225, 3230, 3235, 3240, 3245, 3250, 3255, 3260, 3265, 3270, 3275, 3280, 3285, 3290, 3295, 3300, 3305, 3310, 3315, 3320, 3325, 3330, 3335, 3340, 3345, 3350, 3355, 3360, 3365, 3370, 3375, 3380, 3385, 3390, 3395, 3400, 3405, 3410, 3415, 3420, 3425, 3430, 3435, 3440, 3445, 3450, 3455, 3460, 3465, 3470, 3475, 3480, 3485, 3490, 3495, 3500, 3505, 3510, 3515, 3520, 3525, 3530, 3535, 3540, 3545, 3550, 3555, 3560, 3565, 3570, 3575, 3580, 3585, 3590, 3595, 3600, 3605, 3610, 3615, 3620, 3625, 3630, 3635, 3640, 3645, 3650, 3655, 3660, 3665, 3670, 3675, 3680, 3685, 3690, 3695, 3700, 3705, 3710, 3715, 3720, 3725, 3730, 3735, 3740, 3745, 3750, 3755, 3760, 3765, 3770, 3775, 3780, 3785, 3790, 3795, 3800, 3805, 3810, 3815, 3820, 3825, 3830, 3835, 3840, 3845, 3850, 3855, 3860, 3865, 3870, 3875, 3880, 3885, 3890, 3895, 3900, 3905, 3910, 3915, 3920, 3925, 3930, 3935, 3940, 3945, 3950, 3955, 3960, 3965, 3970, 3975, 3980, 3985, 3990, 3995, 4000, 4005, 4010, 4015, 4020, 4025, 4030, 4035, 4040, 4045, 4050, 4055, 4060, 4065, 4070, 4075, 4080, 4085, 4090, 4095, 4100, 4105, 4110, 4115, 4120, 4125, 4130, 4135, 4140, 4145, 4150, 4155, 4160, 4165, 4170, 4175, 4180, 4185, 4190, 4195, 4200, 4205, 4210, 4215, 4220, 4225, 4230, 4235, 4240, 4245, 4250, 4255, 4260, 4265, 4270, 4275, 4280, 4285, 4290, 4295, 4300, 4305, 4310, 4315, 4320, 4325, 4330, 4335, 4340, 4345, 4350, 4355, 4360, 4365, 4370, 4375, 4380, 4385, 4390, 4395, 4400, 4405, 4410, 4415, 4420, 4425, 4430, 4435, 4440, 4445, 4450, 4455, 4460, 4465, 4470, 4475, 4480, 4485, 4490, 4495, 4500, 4505, 4510, 4515, 4520, 4525, 4530, 4535, 4540, 4545, 4550, 4555, 4560, 4565, 4570, 4575, 4580, 4585, 4590, 4595, 4600, 4605, 4610, 4615, 4620, 4625, 4630, 4635, 4640, 4645, 4650, 4655, 4660, 4665, 4670, 4675, 4680, 4685, 4690, 4695, 4700, 4705, 4710, 4715, 4720, 4725, 4730, 4735, 4740, 4745, 4750, 4755, 4760, 4765, 4770, 4775, 4780, 4785, 4790, 4795, 4800, 4805, 4810, 4815, 4820, 4825, 4830, 4835, 4840, 4845, 4850, 4855, 4860, 4865, 4870, 4875, 4880, 4885, 4890, 4895, 4900, 4905, 4910, 4915, 4920, 4925, 4930, 4935, 4940, 4945, 4950, 4955, 4960, 4965, 4970, 4975, 4980, 4985, 4990, 4995, 5000, 5005, 5010, 5015, 5020, 5025, 5030, 5035, 5040, 5045, 5050, 5055, 5060, 5065, 5070, 5075, 5080, 5085, 5090, 5095, 5100, 5105, 5110, 5115, 5120, 5125, 5130, 5135, 5140, 5145, 5150, 5155, 5160, 5165, 5170, 5175, 5180, 5185, 5190, 5195, 5200, 5205, 5210, 5215, 5220, 5225, 5230, 5235, 5240, 5245, 5250, 5255, 5260, 5265, 5270, 5275, 5280, 5285, 5290, 5295, 5300, 5305, 5310, 5315, 5320, 5325, 5330, 5335, 5340, 5345, 5350, 5355, 5360, 5365, 5370, 5375, 5380, 5385, 5390, 5395, 5400, 5405, 5410, 5415, 5420, 5425, 5430, 5435, 5440, 5445, 5450, 5455, 5460, 5465, 5470, 5475, 5480, 5485, 5490, 5495, 5500, 5505, 5510, 5515, 5520, 5525, 5530, 5535, 5540, 5545, 5550, 5555, 5560, 5565, 5570, 5575, 5580, 5585, 5590, 5595, 5600, 5605, 5610, 5615, 5620, 5625, 5630, 5635, 5640, 5645, 5650, 5655, 5660, 5665, 5670, 5675, 5680, 5685, 5690, 5695, 5700, 5705, 5710, 5715, 5720, 5725, 5730, 5735, 5740, 5745, 5750, 5755, 5760, 5765, 5770, 5775, 5780, 5785, 5790, 5795, 5800, 5805, 5810, 5815, 5820, 5825, 5830, 5835, 5840, 5845, 5850, 5855, 5860, 5865, 5870, 5875, 5880, 5885, 5890, 5895, 5900, 5905, 5910, 5915, 5920, 5925, 5930, 5935, 5940, 5945, 5950, 5955, 5960, 5965, 5970, 5975, 5980, 5985, 5990, 5995, 6000, 6005, 6010, 6015, 6020, 6025, 6030, 6035, 6040, 6045, 6050, 6055, 6060, 6065, 6070, 6075, 6080, 6085, 6090, 6095, 6100, 6105, 6110, 6115, 6120, 6125, 6130, 6135, 6140, 6145, 6150, 6155, 6160, 6165, 6170, 6175, 6180, 6185, 6190, 6195, 6200, 6205, 6210, 6215, 6220, 6225, 6230, 6235, 6240, 6245, 6250, 6255, 6260, 6265, 6270, 6275, 6280, 6285, 6290, 6295, 6300, 6305, 6310, 6315, 6320, 6325, 6330, 6335, 6340, 6345, 6350, 6355, 6360, 6365, 6370, 6375, 6380, 6385, 6390, 6395, 6400, 6405, 6410, 6415, 6420, 6425, 6430, 6435, 6440, 6445, 6450, 6455, 6460, 6465, 6470, 6475, 6480, 6485, 6490, 6495, 6500, 6505, 6510, 6515, 6520, 6525, 6530, 6535, 6540, 6545, 6550, 6555, 6560, 6565, 6570, 6575, 6580, 6585, 6590, 6595, 6600, 6605, 6610, 6615, 6620, 6625, 6630, 6635, 6640, 6645, 6650, 6655, 6660, 6665, 6670, 6675, 6680, 6685, 6690, 6695, 6700, 6705, 6710, 6715, 6720, 6725, 6730, 6735, 6740, 6745, 6750, 6755, 6760, 6765, 6770, 6775, 6780, 6785, 6790, 6795, 6800, 6805, 6810, 6815, 6820, 6825, 6830, 6835, 6840, 6845, 6850, 6855, 6860, 6865, 6870, 6875, 6880, 6885, 6890, 6895, 6900, 6905, 6910, 6915, 6920, 6925, 6930, 6935, 6940, 6945, 6950, 6955, 6960, 6965, 6970, 6975, 6980, 6985, 6990, 6995, 7000, 7005, 7010, 7015, 7020, 7025, 7030, 7035, 7040, 7045, 7050, 7055, 7060, 7065, 7070, 7075, 7080, 7085, 7090, 7095, 7100, 7105, 7110, 7115, 7120, 7125, 7130, 7135, 7140, 7145, 7150, 7155, 7160, 7165, 7170, 7175, 7180, 7185, 7190, 7195, 7200, 7205, 7210, 7215, 7220, 7225, 7230, 7235, 7240, 7245, 7250, 7255, 7260, 7265, 7270, 7275, 7280, 7285, 7290, 7295, 7300, 7305, 7310, 7315, 7320, 7325, 7330, 7335, 7340, 7345, 7350, 7355, 7360, 7365, 7370, 7375, 7380, 7385, 7390, 7395, 7400, 7405, 7410, 7415, 7420, 7425, 7430, 7435, 7440, 7445, 7450, 7455, 7460, 7465, 7470, 7475, 7480, 7485, 7490, 7495, 7500, 7505, 7510, 7515, 7520, 7525, 7530, 7535, 7540, 7545, 7550, 7555, 7560, 7565, 7570, 7575, 7580, 7585, 7590, 7595, 7600, 7605, 7610, 7615, 7620, 7625, 7630, 7635, 7640, 7645, 7650, 7655, 7660, 7665, 7670, 7675, 7680, 7685, 7690, 7695, 7700, 7705, 7710, 7715, 7720, 7725, 7730, 7735, 7740, 7745, 7750, 7755, 7760, 7765, 7770, 7775, 7780, 7785, 7790, 7795, 7800, 7805, 7810, 7815, 7820, 7825, 7830, 7835, 7840, 7845, 7850, 7855, 7860, 7865, 7870, 7875, 7880, 7885, 7890, 7895, 7900, 7905, 7910, 7915, 7920, 7925, 7930, 7935, 7940, 7945, 7950, 7955, 7960, 7965, 7970, 7975

TEMNIKOVA, T.I.; ALMASHI, N.I.

Investigation in the field of cyclic acetals of oxycarbonyl compounds. Part  
5. Methyllactolides of ethylbenzoylcarbinol and methyl- $\alpha$ -anisoylcarbinol.  
Zhur. ob. khim. 23 no.9:1498-1500 S '53. (MLRA 6:10)

1. Laboratoriya im. A.Ye.Favorskogo. Leningradskiy Gosudarstvennyy universitet  
im. A.A.Zhdanova. (Lactolides)

U S S R .

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(2)

Addition of Iodine chloride to 1,1-dichloroethane and  
1,1-diphenylchloroethene. T. T. Pernikova, Z. A. Borkova,  
V. M. Kostylev, V. V. Lutsenko, N. N. Vorotilova.

TEMNIKOVA, T.

USSR/Chemistry - Reaction processes

Card 1/1 Pub. 151 - 21/37

Authors : Temnikova, T., and Myukhyurdari, S.

Title : About anomalous reactions of alpha-bromoketones. Part 4.- Reaction of sodium phenolate with alpha-bromoethylphenylketone.

Periodical : Zhur. ob. khim. 24/10, 1819-1823, Oct 1954

Abstract : The reaction between  $\text{NaC}_6\text{H}_5\text{O}$  and alpha-bromoethylphenylketone was investigated in anhydrous ether and in methyl alcohol. A direct relation between the solvent and the trend of the reaction was established. The products obtained from the reaction of the above mentioned compounds, in an ethyl ether medium and in methyl alcohol, are described. The products derived from the reaction between phenol and methyllactolite of methylbenzoylcarbinol are listed. Eight references: 5-USSR; 2-USA and 1-German (1906-1953).

Institution: State University, Leningrad

Submitted : February 20, 1954

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4"

*V Cyclic acetals of hydroxy carbonyl compounds. VI  
Isomerization of "methyl lactides" of substituted acids into  
methyl ethers of isomeric keto aldehydes.*

*By J. B. Petrucci and S. L. Miller*

*Received May 16, 1955; revised June 1, 1956*

The isomerization of methyl lactide (*Methyl 2-hydroxy-3-oxo-4-oxo-5-oxo-2-phenylpentanoate*) to the derived methyl ether of isomeric keto aldehydes was studied. The methyl ether of 2-hydroxy-3-oxo-4-oxo-5-oxo-2-phenylpentanal was isolated by absorption chromatography. It was obtained by heating in thionyl chloride at 25° for 1 hr. A solution was added to 1 g. Dioxane 10% containing 0.1 g. sodium (in 111.10 mg. which is 52.27% treated with  $\text{MgO Na}$  (from 10 g. Na) suspended in  $\text{Et}_2\text{O}$ ) given 10 hrs. 0.1% *1-methoxy-1-phenyl-2-methyl-1-butene oxide* (*mp* 101–124°,  $\text{d}_{4}^{20} 1.0003$ ,  $n_{D}^{20} 1.5951$ ) also 100 mg. *2-methyl-1-phenyl-1-oxo-3-oxo-4-oxo-5-oxo-2-phenylpentanal* and 243 mg. treating the same way. The yield was 58.6% *Methyl 2-hydroxy-3-oxo-4-oxo-5-oxo-2-phenylpentanal* which may also be isolated by absorption chromatography. The *mp* of the product was 107–110°,  $\text{d}_{4}^{20} 1.0010$ ,  $n_{D}^{20} 1.5958$ . The infrared spectrum showed a strong absorption at 3420 cm<sup>-1</sup> and a very strong absorption at 1720 cm<sup>-1</sup> which was absent in the starting material. The infrared spectrum of *1-methoxy-1-phenyl-2-methyl-1-butene oxide* (*mp* 101–124°,  $\text{d}_{4}^{20} 1.0003$ ,  $n_{D}^{20} 1.5951$ ) was identical with that of the starting material. The infrared spectrum of *2-methyl-1-phenyl-1-oxo-3-oxo-4-oxo-5-oxo-2-phenylpentanal* (*mp* 107–110°,  $\text{d}_{4}^{20} 1.0010$ ,  $n_{D}^{20} 1.5958$ ) was identical with that of the starting material. The infrared spectrum of *1-methoxy-1-phenyl-2-methyl-1-butene oxide* (*mp* 107–110°,  $\text{d}_{4}^{20} 1.0010$ ,  $n_{D}^{20} 1.5958$ ) was identical with that of the starting material.

10.0 g. *Et\_2SO* at above temp. 0.02 M  $\text{NaHCO}_3$  was added and after 10 hrs. the solution was neutralized with 10%  $\text{NaOH}$  and the solution was extracted with  $\text{CHCl}_3$ . The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. The residue was dissolved in  $\text{Et}_2\text{O}$  and dried over  $\text{Na}_2\text{SO}_4$ . The  $\text{Et}_2\text{O}$  was distilled off at 0°C without decomposing the product. The residue was dried in the vacuum desiccator.

10.0 g. *Et\_2SO* at above temp. 0.02 M  $\text{NaHCO}_3$  was added and after 10 hrs. formed *87% MePh-1,1-Me-1,1-phenyl-1-oxo-3-oxo-4-oxo-5-oxo-2-phenylpentanal* (*mp* 107–110°,  $\text{d}_{4}^{20} 1.0010$ ,  $n_{D}^{20} 1.5958$ ). The infrared spectrum of the product was identical with that of the starting material. The infrared spectrum of the starting material was identical with that of the product.

The infrared spectrum of the product was identical with that of the starting material.

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4

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CIA-RDP86-00513R001755220014-4"

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4

*Characteristics of methyl lactolide of crocetin  
Formation and properties of the methyl lactolide of crocetin*

*McOR (cf. C.A. 50, 4781g). Shaking I with dil. H<sub>2</sub>SO<sub>4</sub>*

*Expt. 11. 10 g. 10% Krocetin*

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220014-4"

AUTHORS:

Temnikova, T. I., and Ivanova, V. A.

79-2-14/58

TITLE:

Investigation of Cyclic Acetals of Hydroxy Carbonyl Compounds. Part 8.  
Methyllactolide of Propylbenzoylcarbinol and its Conversions (Issledo-  
vaniye v oblasti tsiklicheskikh atsetaley oksikarbonil'nykh soyedineniy.  
VIII. Metillaktolid propilbenzoilkarbinola i yego prevrashcheniya).

PERIODICAL:

Zhurnal Obshchey Khimii, 1957, vol 27, No 2, pp. 340-342 (U.S.S.R.)

ABSTRACT:

The purpose of this experiment was to study the conversions of methyl-lactolides of alpha-ketoalcohols under the effect of acid reagents in the presence of carbonyl-containing substances and particularly in an acetone solution. The authors wanted to determine whether under such conditions the carbonyl-containing compound will attach itself to the oxide cycle and whether the conversion of the methyllactolide will be the same as in the presence of solvents inactive with respect to the addition reaction in the oxide cycle. The authors obtained and characterized methyllactolide of propylbenzoylcarbinol as an oxide of alpha-methoxy- alpha-phenyl-beta-propylethylene. Methyllactolide dimerizes easily into dioxane derivatives and hydrolyzes into keto-

Card 1/2

79-2-14/58

Investigation of Cyclic Acetals of Hydroxy Carbonyl Compounds. Part 8.  
alcohol-propylbenzoylcarbinol.

Carbinol-containing substances could not be introduced into the reaction with methyllactolide of fatty-aromatic ketoalcohol. The reaction of anhydrous SnCl<sub>4</sub> with methyllactolide led to isomeric conversion of the latter into methyl ether of phenylpropylcarbinol.

There are 8 references, of which 5 are Slavic

**ASSOCIATION:** Leningrad State University

**PRESENTED BY:**

**SUBMITTED:** March 10, 1956

**AVAILABLE:** Library of Congress

Card 2/2

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APPROVED FOR RELEASE: 07/16/2001

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TEMNIKOVA, T.I.; GONTAREV, B.A.

Benzylidene derivatives of the hydrate form of  $\omega$ -ketols  
containing 1,3-dioxolane cycles. Dokl. Akad. Nauk SSSR 112 no.3:  
445-448 Ja '57.

(MLRA 10;4)

1. Leningradskiy gosudarstvennyy universitet im. A.A. Zhdanova.  
Predstavлено академиком I.N. Nazarovym.  
(Ketols) (Toluene) (Dioxolane)

AUTHORS: Temnikova, T. I., Anikeyeva, A. N., SOV/79-28-12-2/41  
Tikhomirova-Sidorova, N. S.

TITLE: S. N. Danilov's Work in the Field of Isomeric Transformations  
and Molecular Regroupings of Carbonyl, Oxy-Carbonyl Compounds  
and Carbohydrates, and Their Theoretical Importance (Raboty  
S. N. Danilova v oblasti izomernykh prevrashcheniy i  
molekulyarnykh peregruppirovok karbonil'nykh, oksikarbonil'nykh  
soyedineniy i uglevodov i ikh teoreticheskoye znacheniye)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 12,  
pp 3162-3173 (USSR)

ABSTRACT: Since Danilov's first work 45 years ago there has taken place  
a great change in theory concerning the problem of the  
molecular regroupings and isomeric transformations of oxygen-  
containing compounds; this was mainly due to Danilov's and  
his cooperators' work. At present it is taken for sure that  
molecular regroupings which complicate chemical processes  
in organic chemistry, depend kinetically on the displacement  
of the hydrogen atoms or the carbohydrate group into the  
adjacent position. The isomeric equilibrium transformations,  
which take place very easily in some cases under the influence

Card 1/3

S. N. Danilov's Work in the Field of Isomeric Transformations and Molecular Regroupings of Carbonyl, Oxy-Carbonyl Compounds and Carbhydrates, and Their Theoretical Importance

SOV/79-28-12-2/41

of the catalysts favorable to these transformations, depend, like all equilibrium processes, on thermodynamic factors. According to detailed reports published by Danilov important conditions are mentioned that must be taken into consideration in interpreting the mechanism of molecular regroupings of the  $\alpha$ -glycols. The basic idea throughout all his papers is that the process of transformation depends not only on the radicals but also on their interaction, on the dehydrating agent and on conditions under which the dehydration takes place. He and his cooperators systematically investigated the behavior of  $\alpha$ -oxy-aldehydes under the action of various catalysts, which led to important results. The oxy-aldehyde-oxy-ketone regrouping in acid medium according to Danilov takes place under an intermediate formation of  $\alpha$ -alcohol oxides (scheme on page 3167). The manifold types of isomeric transformations and molecular regroupings were illustrated by Danilov with supplementary informations offered by other scientists according to the scheme of transitions of genetically related

Card 2/3

S. N. Danilov's Work in the Field of Isomeric Transformations and Molecular Regroupings of Carbonyl, Oxy-Carbonyl Compounds and Carbohydrates, and Their Theoretical Importance

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compounds as mentioned on page 3169 (upper half); this was carried out, for instance, in the case of compounds with two phenyl groups and two carbon atoms in the chain (the big arrows point to the transformation types realized by him). The logical continuation of the investigations of the transformations of  $\alpha$ -oxy-carbonyl compounds were his manifold papers on the monoses and disaccharides, "a", for instance, those on a new method for the "epimerization" of sugars. He and his cooperators synthesized a large number of derivatives of multivalent alcohols, their aldehydes and monoses. Based on an intramolecular simultaneous acid-alkaline reaction process found by him in a large number of reactions he could explain many biochemical processes of nature. There is 1 table.

Card 3/3

AUTHORS:

Temnikova, T. I., Oshuyeva, N. A.

SOV/79-28-12-13/41

TITLE:

Chemical Transformations of  $\alpha$ -Halogen Ketones (Khimicheskiye prevrashcheniya  $\alpha$ -halogenketonov) VI. Action of Sodium Phenolate and Cresylate on  $\alpha$ -Bromo-Cyclohexanone (VI. Deystviye fenolyata i krezolyata natriya na  $\alpha$ -bromtsiklogekanon)

PERIODICAL:

Zhurnal obshchey khimii, 1958, Vol 28, Nr 12, pp 3224-3226 (USSR)

ABSTRACT:

Continuing earlier papers (Ref 1) this paper deals with the reaction of sodium phenolate and -p-cresylate with  $\alpha$ -bromo-cyclohexanone in methyl alcohol solution. The problem was whether also in the cyclohexanone series the formation of mixed ketals could be found, which would indirectly point to the formation of phenyl "lactolides" in this series. Ebel (Ebel') (Ref 3) was the first to carry out this reaction in petroleum ether, and he obtained a product with the melting-point of 64-65°, of the empirical formula  $C_{12}H_{14}O_2$ . In the beginning he looked upon it as a phenoxy cyclohexanone, which, however, he later substituted for the phenoxy oxide, based on the hydrolysis with phenylhydrazine. The authors obtained again the same product following Ebel's method, with the only

Card 1/3

Chemical Transformations of  $\alpha$ -Halogen Ketones.  
VI. Action of Sodium Phenolate and Cresylate on  
 $\alpha$ -Bromo-Cyclohexanone

SOV/79-28-12-13/41

difference that the sodium bromide was separated by centrifuging and not by water; this was done to avoid a decomposition of the phenyl "lactolide" to be expected. Ebel's product melting at 65° was spectrochemically investigated and its absorption spectra pointed to a carbonyl and phenyl group. Thus, the initial idea of Ebel (Formula I =  $\alpha$ -phenoxy cyclohexanone) was proved, which could also be supported by the hydrolysis of the product with 2,4-dinitro-phenyl hydrazine, as opposed to the second idea, in the form of 2,4-dinitro-phenyl hydrazone. The reaction of sodium phenolate with  $\alpha$ -bromo-cyclohexanone was no longer carried out in petroleum ether by the authors (according to Ebel), but in methyl alcohol, and they obtained the methyl-phenyl ketal of cyclohexanol (II); this ketal is extremely unstable and requires special precaution in its distillation to obtain an analytical-pure form. On the action of p-sodium cresylate on  $\alpha$ -bromo-cyclohexanone in methyl alcohol also a highly unstable methyl-p-cresyl ketal of cyclohexanol was obtained. There are 6 references, 3 of which are Soviet.

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Chemical Transformations of  $\alpha$ -Halogen Ketones.  
VI. Action of Sodium Phenolate and Cresylate on  
 $\alpha$ -Bromo-Cyclohexanone

SOV/79-28-13/41

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State  
University)

SUBMITTED: December 31, 1957

Card 3/3

TEMNIKOVA, Tat'yana Ivanovna; KHAVIN, Z.Ya., red.; SHUR, Ye.I., red.;  
ERLIKH, Ye.Ya., tekhn.red.

[Theoretical fundamentals of organic chemistry] Kurs teore-  
ticheskikh osnov organicheskoi khimii. Leningrad, Gos.nauchno-  
tekhn.izd-vo khim.lit-ry, 1959. 808 p.  
(MIRA 12:8)  
(Chemistry, Organic)

SOV/79-2-7/7<sup>1</sup>

AUTHORS: Temnikova, T. I., Kovalevskaya, R. N., Matveyenkova, N. I.,  
Sklyarova, V. V.

TITLE: Investigation in the Field of Cyclic Acetals of Oxy-carbonyl Compounds (Issledovaniye v oblasti tsiklicheskikh atsetaley oksikarbonil'nykh soyedineniy). IX. Ethyl Lactolides and Diethyl Ketals of Ethyl-benzoyl Carbinol and Propyl-benzoyl Carbinol (IX. Etillaktolidy i dietilketali etilbenzoilkartinola i propilbenzoilkartinola)

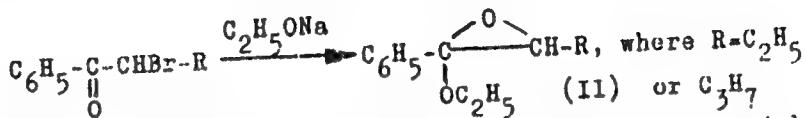
PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 381-386 (USSR)

ABSTRACT: Investigation of ethyl lactolides of the  $\alpha$ -keto alcohols has been hitherto very scarce. Following up earlier papers by Temnikov and collaborators, as well as of other chemists, the present paper describes the synthesis of two new ethyl lactolides of the secondary aliphatic-aromatic  $\alpha$ -keto alcohols, ethyl-benzoyl carbinol and propyl-benzoyl carbinol. On carrying out the reaction in the usual way, i.e. by the action of a suspension of sodium ethylate in absolute ether, resinification occurred:

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SOV/79-29-2-7/71

Investigation in the Field of Cyclic Acetals of Oxy-carbonyl Compounds.  
IX. Ethyl Lactolides and Diethyl Ketals of Ethyl-benzoyl Carbinol and Propyl-benzoyl Carbinol



Both ethyl lactolides (yield 10-15%) are very unstable and immediately yield ethyl-benzoyl carbinol with water in an alkaline medium. On the action of sodium ethylate upon the same bromo-ketones in absolute alcohol resinification is insignificant; still, only with  $\alpha$ -bromo-butyl-phenyl ketone the separation of the corresponding lactolide ( $\text{II}, \text{R}=\text{C}_3\text{H}_7$ ) was successful. On standing, however, either diethyl ketals of the corresponding  $\alpha$ -keto alcohols (III) or further transformation products are formed. Thus, on the action of sodium ethylate on  $\alpha$ -bromo-propyl-phenyl ketone not diethyl ketal is formed but a lactolide of ethyl-benzoyl carbinol ( $\text{IV}, \text{R}=\text{C}_2\text{H}_5$ ). Diethyl ketals ( $\text{III}, \text{R}=\text{C}_2\text{H}_5$  or  $\text{n}-\text{C}_3\text{H}_7$ ) are obtained at low temperature only. In analytically

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Investigation in the Field of Cyclic Acetals of Oxy-carbonyl Compounds.  
IX. Ethyl Lactolides and Diethyl Ketals of Ethyl-benzoyl Carbinol and Propyl-benzoyl Carbinol

pure state only diethyl ketal of ethyl-benzoyl carbinol was obtained, which is likewise very unstable. Ethyl lactolides are much more unstable than methyl lactolides of the same keto alcohols. On the action of  $ZnCl_2$  on the ethyl lactolide of propyl-benzoyl carbinol, a dimerization takes place in the cyclodiethyl dilactolide. There are 10 references, 6 of which are Soviet.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State University)

SUBMITTED: December 31, 1958

Card 3/3

*TEMNIKOVA, T.I.*

## TABLE I WORK BIBLIOGRAPHY

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- Karp, R. I. *T.A. Fominykh* Ed.: V.D. Platonov, Publ. Ed.: S.D. Todorov.
- Fominykh, T.A. This collection of articles is intended for chemists and organic chemists.
- Comments: The collection is connected with the scientific legacy of A.T. Fominykh. The collection documents all theoretical ideas and their evolution in connection with the development of organic chemistry. The articles present the problems on the structure, reactivity and transformations of various classes of organic compounds: aromatic, cyclic and cyclic hydrocarbons, saturated and unsaturated hydrocarbons, aromatic and carbonyl compounds. To permeation and maturation, references are given to each article.
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- Terpenoids. 125. Participation of Repeating Groups in Chemical Processes. 210
- Terpenoids. 125. Participation of Repeating Groups in Chemical Processes. 210
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5.3400.

78257  
SOV/79-30-3-11/69

AUTHORS: Temnikova, T. I., Gissel', R., Gontarev, B. A.

TITLE: Investigation in the Field of Cyclic Acetals of Oxycarbonyl Compounds. X. Methyl Lactolides of Dimethyl-p-Anisoyl- and Dimethyl-p-Chlorobenzoyl Carbinols and Their Transformations

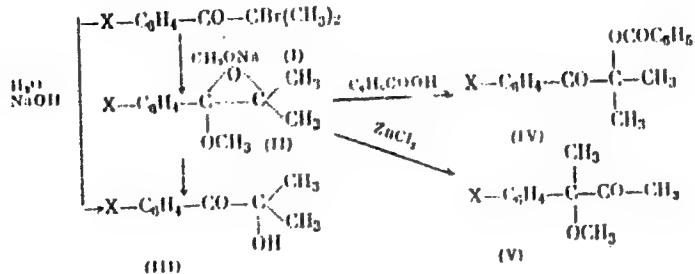
PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 3,  
pp 776-781 (USSR)

ABSTRACT: Two methyl lactolides of tertiary aliphatic-aromatic  $\alpha$ -keto alcohols with Cl- and  $\text{CH}_3\text{O}$ -substituted benzene ring were synthesized.  $\alpha$ -Bromoisopropylanisyl ketone (I,  $X = \text{CH}_3\text{O}$ ) on slow heating with sodium methylate gave an oily substance, which, on vacuum distillation and fractionation, gave the methyl lactolide of dimethyl-p-anisoyl carbinol (II,  $X = \text{CH}_3\text{O}$ ; bp  $84^\circ \text{C}$  at 2 mm;  $97^\circ \text{C}$  at 4 mm;  $108.5^\circ \text{C}$  at 6 mm; mp  $38.5-39^\circ \text{C}$ ).

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Investigation in the Field of Cyclic  
Acetals of Oxycarbonyl Compounds. X

78257  
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Methyl lactolide of dimethyl-p-chlorobenzoyl carbinol

(II,  $X = \text{Cl}$ , bp  $94-95^\circ\text{C}$  at 5 mm) was obtained similarly from  $\alpha$ -bromoisopropyl-p-chlorophenyl ketone (I,  $X = \text{Cl}$ ). Both lactolides were comparatively stable and did not decompose in sealed ampoules for a long period of time. They were hygroscopic and hydrolyzed in air forming the corresponding  $\alpha$ -keto alcohols (III). The methoxy-substituted lactolide was much more hygroscopic and hydrolyzed more easily than the chlorine-substituted

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Investigation in the Field of Cyclic  
Acetals of Oxycarbonyl Compounds. X

100-11  
309/79-30-3-11/69

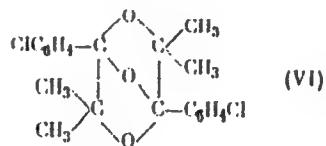
one. The lactolides in reaction with benzoic acid gave the corresponding esters (IV; mp 75.5-74.5° C, from petroleum benzin, for X = CH<sub>3</sub>O, mp 110-111° C, from aqueous methanol, for X = Cl). Heating with a small amount of ZnCl<sub>2</sub> isomerized the lactolides into the corresponding methoxy ketones (V, bp 102-103° C at 2.5 mm; mp 41-42° C, for X = CH<sub>3</sub>O; bp 118-119° C at 9 mm for X = Cl). Carbinol (III, X = CH<sub>3</sub>O, mp 54-55° C) was also obtained on heating the bromoketone I with aqueous NaOH or on hydrolysis of the methyl lactolide with H<sub>2</sub>SO<sub>4</sub>, also with heating. The introduction of Cl-substituent in para-position of the benzene ring speeded up the reactions as compared with unsubstituted or CH<sub>3</sub>O-substituted compounds. The bromoketone (I, X = Cl) gave with NaOH a highly exothermal reaction yielding carbinol (III, X = Cl, bp 115-117° C). The latter

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Investigation in the Field of Cyclic  
Acetals of Oxycarbonyl Compounds. X

78257  
SOV/79-3-11/69

was very unstable and in the presence of acids was  
transformed into the anhydrotomer (VI, mp 177-178° C,  
from aqueous methanol) of a presumably tricyclic  
structure.



There are 9 references, 2 U.S., 1 German, 6 Soviet.  
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J. Am. Chem. Soc., 76, 2506 (1954); A. K. Glasgow,  
G. Ross, J. Res. NBS, 57, Nr 5 (1956).

ASSOCIATION: Leningrad State University (Leningradskiy gosudarstvennyy universitet)

SUBMITTED: July 22, 1959  
Card 4/4

TEMNIKOVA, T.I.; GONTAREV, B.A.; GISSEL', R.

Cyclic acetals of hydroxy carbonyl compounds. Part 11: Interaction  
between methyl lactolides of fatty-aromatic  $\alpha$ -keto alcohols and  
aromatic aldehydes and ketones. Zhur. ob. khim. 30 no.8:  
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(Aldehydes) (Ketones) (Alcohols)

TEMNIKOVA, T.I.; CHERKASOVA, V.A.; PIASTRC, V.D., red.; KISELEVA, L.I.,  
tekhn. red.

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Reactions of sodium acetoacetate with  $\alpha$ -oxybromides. Zhur. ob.  
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1. Leningradskiy gosudarstvennyy universitet imeni A.A.  
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(Chemistry, Organic)

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1. Leningradskiy gosudarstvennyy universitet.  
(Acetals) (Ketones)

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TEMNIKOVA, T.I., prof.

Structure of molecules and molecular rearrangements. Zhur. VYHO  
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(Chemical structure) (Rearrangements (Chemistry))

TEMNIKOVA, T.I.; YERSHOV, B.A.

Reactions of methylbenzoylcarbinol and ethylbenzoylcarbinol  
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32 no.2:661-662 F '62. (MIRA 15:2)

1. Leningradskiy gosudarstvenny universitet.  
(Alcohols)  
(Acetoacetic acid)

TEANIKOVA, T.I.; YERSHOV, B.A.

Interaction of metal derivatives of  $\beta$ -dicarbonyl compounds with  
 $\alpha$ -halogen oxides. Part 1: Interaction of Na- and  $C_6H_5CH_2(CH_3)_3$   
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1. Leningradskiy gosudarstvennyy universitet.  
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$\beta$ -Hydroxy- and  $\beta$ -halo carbonyl compounds. Part 2: Preparation of aliphatic-aromatic  $\beta$ -ketols substituted in the nucleus. Zhur. ob. khim. 33 no. 5:1403-1404 My '63.

(MIRA 16:6)

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TEMNIKOVA, T.I.; YERSHOV, B.A.

Reactions of metallic derivatives of  $\beta$ -dicarbonyl compounds  
with  $\alpha$ -halooxides. Part 2: Reaction of Na-dimedon with  
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1. Leningradskiy gosudarstvennyy universitet.  
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(Epibromohydrin)